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ABSTRACT

Title:	Characterization and Optimization of a High Surface Area-Solid Phase Microextraction Sampler for the Collection of Trace Level Volatile Organic Compounds in the Field
	Shannon Scott McDonald, Master of Science in Public Health, 2006
Directed By:	Gary Hook, CDR, USN Assistant Professor, Department of Preventive Medicine and Biometrics

A prototype rapid, high volume air sampling device based on Solid Phase Microextraction (SPME) has been developed for the collection of trace level volatile organic compounds (VOCs). The High Surface Area-Solid Phase Microextraction (HSA-SPME) device contains ten times more polymer than traditional SPME fibers and is uniquely designed to optimize compound uptake at higher flow rates. This study evaluated the extraction efficiency at six air sampling flow rates ranging from 0.1 L/min to 10 L/min and compared total compound extraction at the two extreme flow rates. A 10 ppb_v concentration of 39 volatile organic compounds was used. Carboxen/Poly(dimethylsiloxane) and Poly(dimethylsiloxane) polymer coatings were evaluated using an Agilent 6890N/5973, a resistively heated Low Thermal Mass Gas Chromatograph column and an Entech 7100 Preconcentrator. Larger extraction efficiencies were observed at lower flow rates, but the higher flow rates proved superior in total compound extraction per unit time. Across the range of compounds, the HSA-SPME device achieved an average 8-fold increase in compound uptake at a flow rate of 10 L/min as compared to 0.1 L/min.

Characterization and Optimization of a High Surface Area-Solid Phase Microextraction Sampler for the Collection of Trace Level Volatile Organic Compounds in the Field

By

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Thesis submitted to the Faculty of the Graduate School of the
Uniformed Services University of the Health Sciences in partial fulfillment
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Master of Science in Public Health

2006

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This study is dedicated to my beautiful wife, Jennifer.

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Table of Contents

List of Figures

List of Tables

List of Symbols and Abbreviations

BTEX	Benzene, toluene, ethyl benzene, xylene
CAS	Chemical Abstract Number
cm	Centimeter
cm/sec	Centimeters per second
CWA	Chemical Warfare Agent
D_f	Film thickness
EPA	Environmental Protection Agency
eV	Electron volt
GC/MS	Gas Chromatography / Mass Spectrometry
HSA-SPME	High surface area-solid phase microextraction
i.d.	Inner diameter
L	Liters
L/min	Liters per minute
L/sec	Liters per second
LTMGC	Low Thermal Mass Gas Chromatograph
m	Meter
mg/m^3	Milligrams per cubic meter
min	Minute
mm	Millimeters
mph	Miles per hour
o.d.	Outer diameter
PDMS	Poly(dimethylsiloxane)
ppb_v	Parts per billion by volume
ppm_v	Parts per million by volume
sec	Seconds
SPME	Solid Phase Microextraction
TM	Trade mark
TO-14	Toxic Organics-14
µm	Micrometers or “Micron”
$µm/cm^3$	Micrometers or “Micron” per cubic centimeter
V	Volt
VOCs	Volatile Organic Compounds
VOIs	Volatile Organic Impurities

1 Introduction

1.1 Background

Rapid, on-site chemical analysis is advantageous to a large number of organizations. Military personnel tasked with detection of chemical warfare agents (CWAs) require rapid chemical identification to alert and protect soldiers and civilians. Federal and local authorities responding to hazardous material emergencies also need rapid chemical identification to protect the public and responders. The Federal Bureau of Investigation (FBI) or other law enforcement agencies need to be able to rapidly identify explosives, narcotics, human scent and other compounds for crime scene investigations. Industry and environmental regulators can save time and money by expediting compliance sampling at hazardous waste sites or process modifications. Several advances to aid in rapid, on-site analysis include field portable GC/MS, resistively heated low thermal mass GC (LTMGC) columns, and solid phase microextraction (SPME). This study incorporates these advances and characterizes the efficiencies, both for sampling and desorption, of a new prototype air sampling device, known as a High Surface Area-Solid Phase Microextraction (HSA-SPME) device using a variety of volatile organic compounds (VOCs).

One of the most powerful tools in identifying unknown VOCs in the environment is Gas Chromatography – Mass Spectrometry (GC/MS) (Schuetz 1995; Smith 2002). GC/MS instruments were once confined only to laboratories, but now these instruments have become more rugged, smaller and require less power; thereby allowing their use directly in the field. Using GC/MS in the field provides definitive on-site chemical analysis. GC/MS identifies compounds in two ways. First the compound is separated in

the GC column and the amount of time the compound takes to get through the column (known as retention time) provides some information on compound identification. After the GC column, the compound is exposed to an electron beam in the MS, which fractionates the compound into primarily charged fragments. These ion fragments and the distribution of the ion mass-to-charge ratios (*m/z*) are compared to a library for identification. Both retention time and the ion fragment mass spectrum provide a high degree of certainty in identifying an unknown compound or aid in verifying a known or targeted compound.

A recent development in GC is the LTMGC column. Unlike traditional GC ovens, the LTMGC heats the column using a resistively heated nickel-chromium alloy that helps drive compounds through the column. Traditional GC/MS instruments use an air bath oven and convection to heat the column. GC ovens are large, require a lot of power, and are generally slow. The LTMGC resistive heating substantially reduces the weight and power requirements and allows better control of the GC column temperatures as compared to a traditional air bath oven (Sloan 2001; Whitchurch 2003). LTMGC columns improve the operational capabilities of GC/MS systems making them more field usable.

Another development that has helped to advance field detection is the use of SPME fiber samplers. SPME is a polymer material usually attached to a 1 centimeter (cm) fused silica fiber that extracts compounds from the environment. Traditional sample collection techniques often involve collecting samples in Tedlar™ bags or passing air through an adsorbing media such as charcoal, and then desorbing the compounds from the media into a solvent for analysis. The wet chemistry involved, as

well as handling, storage and transportation, generates significant amounts of solvent waste, is time consuming and labor intensive, which increase the risk of introducing sample bias or losses. SPME fiber technology provides a collection technique that virtually eliminates sample preparation and allows direct sample introduction into analytical instrumentation.

SPME fibers have some limitations, which can be attributed to their size. SPME fibers are fused silica rods typically only 1-2 cm long with a 110 μm outer diameter. The SPME polymer coatings that surround the rod typically range in thickness from 0.7 to 100 μm, resulting in a small surface area that limits the mass of analyte that can be extracted from the environment. To extract more analyte mass, the SPME fiber can remain exposed to the environment for a longer period of time, but this is counterproductive to the goal of rapid field sampling. Additionally, SPME fibers are typically passive samplers meaning they rely on natural air currents to extract compounds from the environment.

A recent enhancement of SPME is the prototype HSA-SPME air sampling device. The HSA-SPME device is approximately 10 times larger than traditional SPME fibers and utilizes dynamic air sampling (pulling air across the SPME polymer via a pump). The HSA-SPME is designed inside a glass tube forcing air across the SPME polymer and enhancing analyte mass transfer. The HSA-SPME unique design, larger polymer surface area, and the use of dynamic sampling increases compound extraction and allows faster, larger sample volume collection with better sensitivity than traditional SPME fibers (Ramsey 2004).

1.2 Research Question and Specific Aims

Does compound extraction efficiency increase as linear velocity increases through the HSA-SPME device, and do higher linear velocities offer an advantage for sampling trace level VOCs?

1. Develop analytical method for HSA-SPME and GC/MS for the detection of VOCs in air.
2. Measure extraction efficiency for the HSA-SPME device at six flow rates using a 10 parts per billion by volume (ppb_v) concentration of 39 compounds.
3. Compare total compound extraction at highest and lowest flow rates for a 10 second sample at 10 ppb_v for 39 compounds.
4. Test two HSA-SPME polymer types (Poly(dimethylsiloxane) (PDMS) and Carboxen/PDMS combination) for longevity and durability.

1.3 Compound Extraction and Desorption Defined

Two terms used throughout this research that need to be defined are extraction efficiency and desorption efficiency. Extraction efficiency is a measure of how well the HSA-SPME polymer coating traps compounds out of the air at ambient temperature. Desorption efficiency, on the other hand, is a measure of how well the compounds are released from the HSA-SPME polymer when heated. Compounds are first extracted with the polymer coating from the environment and then desorbed into analytical instrumentation.

2 Literature Review

Three areas are combined in this research: HSA-SPME Air Sampling Devices, GC/MS and LTMGC resistively heated columns. Each technology is discussed in this chapter.

2.1 Solid Phase Microextraction Theory

HSA-SPME uses SPME polymers in a modified design to extract compounds from the environment and is therefore fundamentally based on SPME theory. SPME is generally a passive sampling technique based on analyte partitioning and the principle of "like dissolves like." In the environment, chemicals move in and out of environmental matrices based on their affinity for the different matrices. If a specific compound has a greater affinity for a particular matrix, based on polarity for example, that compound will favor partitioning into that matrix. SPME polymers impart a strong polar or non-polar force to extract compounds with similar polarity from the environment (Pawliszyn 1997).

SPME fibers are commercially available with several types of polymer coatings having different thicknesses, porosity, and polarity. The thickness and porosity of the polymer coating affect the mass quantity and molecular size of the compounds extracted. Polarity, boiling point, and to some degree molecular weight are chemical properties that contribute to compound extraction by SPME fibers. PDMS is the most common non-polar fiber coating, and Polyacrylate and Carbowax are common polar coatings. Fiber coatings also come in mixtures, such as Divinylbenzene and Carboxen. Various combinations of the fiber coatings can be created (with differing thickness and porosity) to optimize the performance of SPME collection and accommodate various sampling situations (Pawliszyn 1997).

SPME fiber sampling techniques have been studied and used extensively in a variety of disciplines, such as industrial hygiene, environmental compliance, pharmaceutical industry, indoor air quality, criminal investigations, and military and disaster response scenarios. SPME fibers have proven useful for the detection of a large range of volatile and semi-volatile compounds from nearly all environmental matrices: air, wastewater, drinking water, soil, etc. SPME fibers demonstrated the ability to detect over 60 VOCs using a dynamic air sampling technique in a swine building environment with an air sampling flow rate of 100 mL/min for 60 minutes (Razote 2002). SPME fibers were also used in Dhaka City, Bangladesh to monitor airborne VOC emission from two-stroke autorickshaw engines and automobiles detecting over 200 hydrocarbon compounds and achieving limits of detection around 1 $\mu g/m^3$ for most of the semi-volatiles (Hussam 2002). SPME fibers have also been used in the analysis of nuclear weapons from manufacturing quality control monitoring to weapon degradation products (Chambers 1998). One study applied environmental sampling with SPME fibers during a massive aircraft accident (Hook 2002). During the aircraft fire response, SPME sampling served as a rapid field screening tool that later guided quantitative laboratory analyses and reduced complete site characterization to less than two days.

SPME fiber sampling has been used on several occasions to detect the presence of CWAs. One study demonstrated a field expedient analytical method to detect sulfur mustard in contaminated soil using SPME headspace sampling (Kimm 2002). With the same SPME technique, another study demonstrated a safe analytical method to identify VX contamination in soil by targeting a degradation by-product of VX called bis(diisopropylaminoethyl)-disulfide (Hook 2003). Another study demonstrated the

ability to detect the CWAs sarin, soman, sulfur mustard, and cyclohexyl-methylphosphonofluoride while comparing instrument and sampling strategies (Smith 2004). In another study, dynamic SPME fiber sampling was used to detect airborne sarin (Hook 2003). This study found an increased efficiency with increased air velocity across the fiber over the traditional passive sampling technique.

SPME fibers have proven useful in several forensic applications, such as criminal investigations and narcotic toxicology. SPME fibers have been used for trace level detection of ignitables and accelerants from fire debris in arson investigations and explosives residue from bombing scenes (Scheppers-Wercinski 1999). SPME fibers have displayed the ability to concentrate organic or inorganic compounds of interest from complex matrices with relatively clean extractions and low detection limits. SPME fibers have also proven useful in clean extraction of narcotics and poisons from body fluids (Scheppers-Wercinski 1999). More recent research in forensic application of SPME fibers is in human scent detection, identification, and verification to mimic canine scent detection capabilities. SPME fiber's ability to extract volatile compounds from forensic specimens provides possibilities in understanding canine odor detection (Norma Lorenzo 2003). It is this last area of research that has led to the development of the HSA-SPME device with hopes to achieve rapid, large volume air sampling with the ease of SPME fiber theory.

The pharmaceutical industry has begun to use SPME fibers for the detection and monitoring of volatile organic impurities (VOIs) to ensure quality, purity, and potency in the manufacturing process (Scheppers-Wercinski 1999). The five regulated VOIs monitored by SPME fibers are methylene chloride, chloroform, benzene,

trichloroethylene, and 1,4-dioxane. Other potential applications for the pharmaceutical industry include biological monitoring to determine drug metabolism rates. SPME fibers have also proven useful in monitoring and researching food additives and flavoring. All these applications require the detection of trace level compounds.

2.2 High Surface Area – Solid Phase Microextraction Air Sampling Device

The HSA-SPME device contains a SPME polymer coating, therefore relies on compounds partitioning from the environment to the coating. Figure 2-1 displays a computer generated cross-sectional view of the HSA-SPME device. The HSA-SPME device consists of a nickel alloy wire 100 mm long with a diameter of 0.127 mm and is coated with a solid sorbent SPME polymer. The coated wire is helically wrapped around a small borosilicate glass tube (50 mm x 1.2 mm o.d.), and positioned inside a larger borosilicate glass tube (78.5 mm x 3.0 mm i.d.). The inner glass tube provides some physical support to the wire while the outer glass tube protects the entire device. The nickel alloy wire and SPME polymer are located in the space between the two glass tubes, which is referred to as the annular space. As air flows through the restrictive annular space, the “air flow theoretically conforms primarily to a rotational motion characteristic of the helical design," forcing the compounds to come into continuous contact with the SPME polymer down the length of the inner tube (Ramsey 2006). The nickel alloy wire is connected at each end by electrical wires for resistive heating via a controlled current power supply, which desorbs the compounds from the polymer. Note the difference from traditional SPME. Any standard SPME coating can be used on the nickel alloy wire; however, the coating must be flexible enough to be wrapped around the

inner glass tube and thin enough to fit inside the outer glass tube. As shown in Figures 2-1, the design of the HSA-SPME sampling device allows air to be drawn through the annular space between the outer and inner glass tubes. Figure 2-2 displays the key components of the HSA-SPME device.

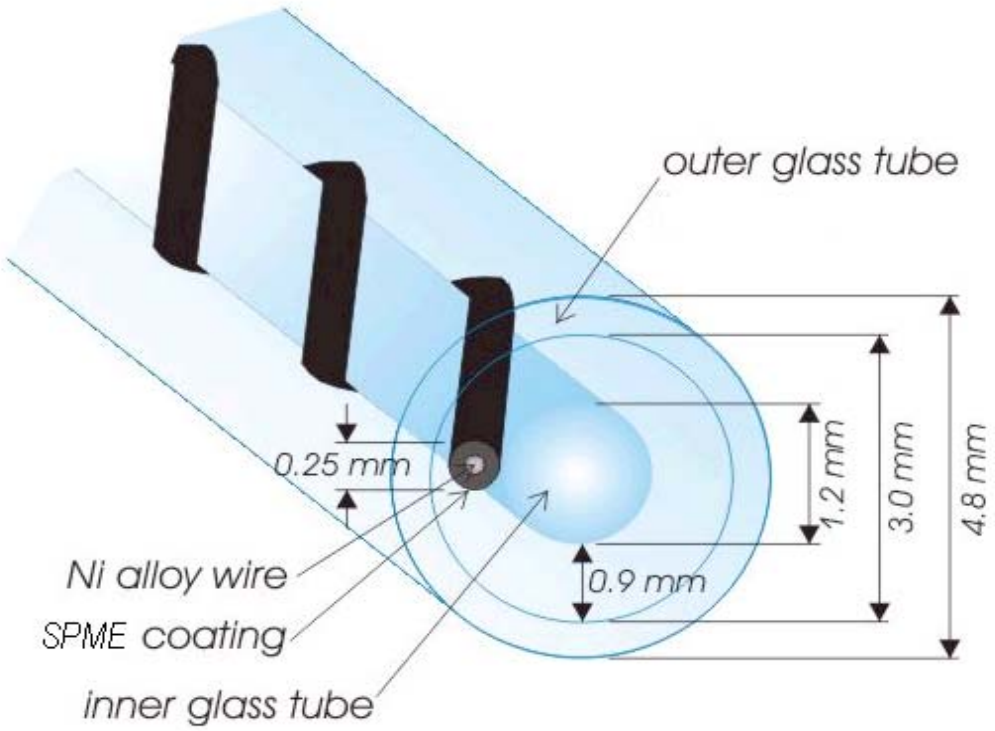


Figure 2-1: Computer Generated Cross Sectional View of HSA-SPME Device

One early study that explored the idea of continuous air monitoring with a helical sorbent microtrap, similar to the HSA-SPME device, consisted of a 0.07 mm diameter chromium-aluminum alloy wire wrapped around a 0.1 mm diameter straight wire. The

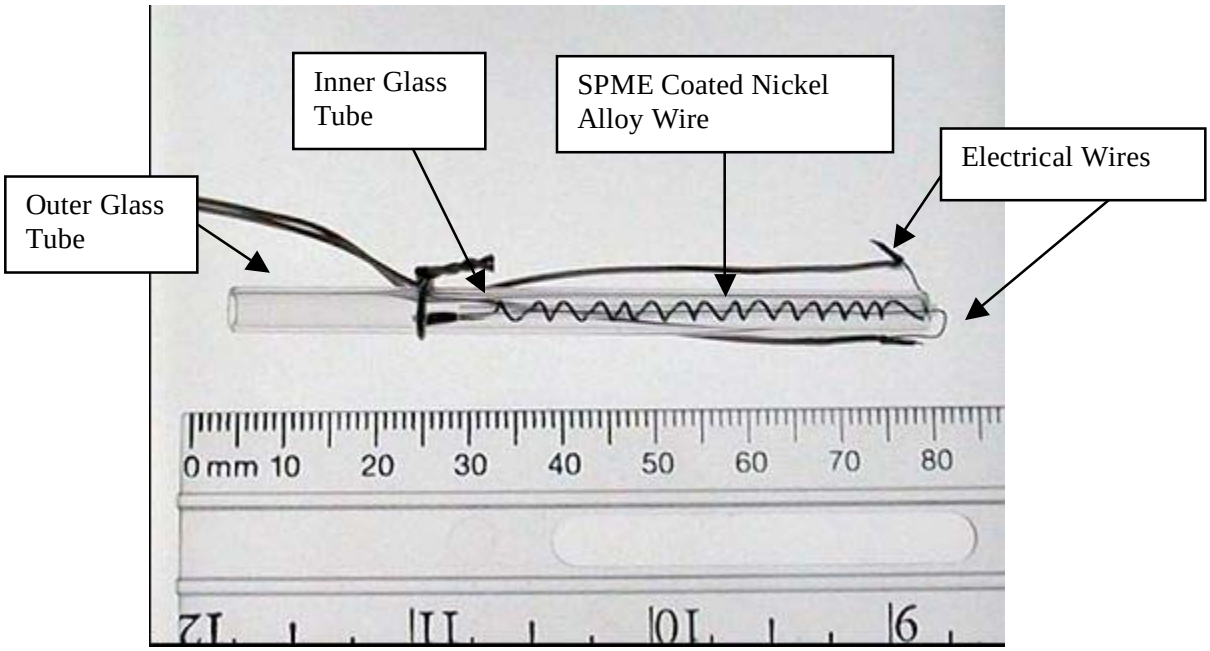


Figure 2-2: High Surface Area-Solid Phase Microextraction Device (Ramsey 2004)

sorbent microtrap was then dipped and baked several times in a PDMS polymer, and placed inside a silicosteel capillary tube. Compounds were desorbed via forced heat convection between the silicosteel capillary tube and the carrier gas flow, and analyzed by a GC with a flame ionization detector. The authors demonstrated this technique in a continuous on-line system where the compounds were continuously collected and concentrated, and periodically desorbed and analyzed (Ciucanu 2003).

To date, only one study has been conducted with HSA-SPME devices (Ramsey 2004). The study used a laboratory GC and a micro-pulsed discharged helium ionization detector to compare the HSA-SPME device to both passive and dynamic SPME fiber sampling techniques. Referring to Figure 2-3, compound extraction with the HSA-SPME was "one order of magnitude greater than both the passive and dynamic SPME techniques, and yielded a 1-2 orders of magnitude lower detection limit (Ramsey 2006)."

This study used a short list of target compounds: benzene, toluene, ethyl benzene, and m-, p-, and o-xylene (BTEX). The dynamic sampling parameters were 2.1 L/min for 15 seconds, and the passive parameters consisted of a 2-minute SPME fiber static exposure.

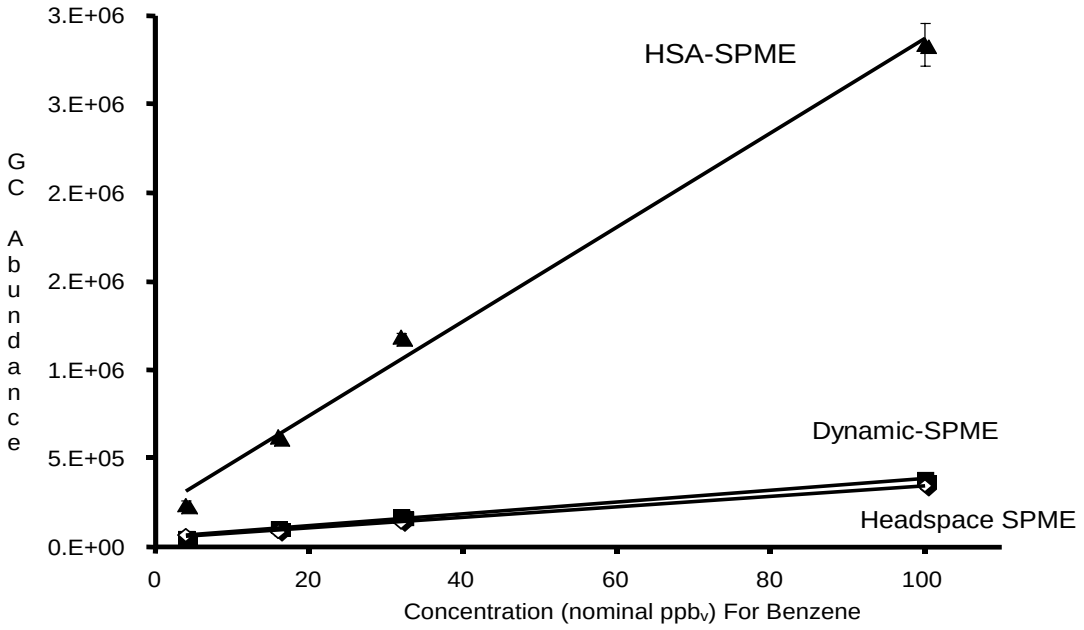


Figure 2-3: HSA-SPME With Static and Dynamic SPME Comparison (Ramsey 2006)

The study also determined if compound uptake reached a maximum extraction potential as linear velocities through the HSA-SPME increased. A dramatic increase in compound uptake was evident as linear velocity approached 40 cm/sec (see Figure 2-4). A second increase in compound uptake was also identified with linear velocities greater than 350 cm/sec. A 65 μm Carboxen/PDMS HSA-SPME device was used in this experiment with a constant sampling time of 15 seconds using a 40 ppb_v concentration of BTEX.

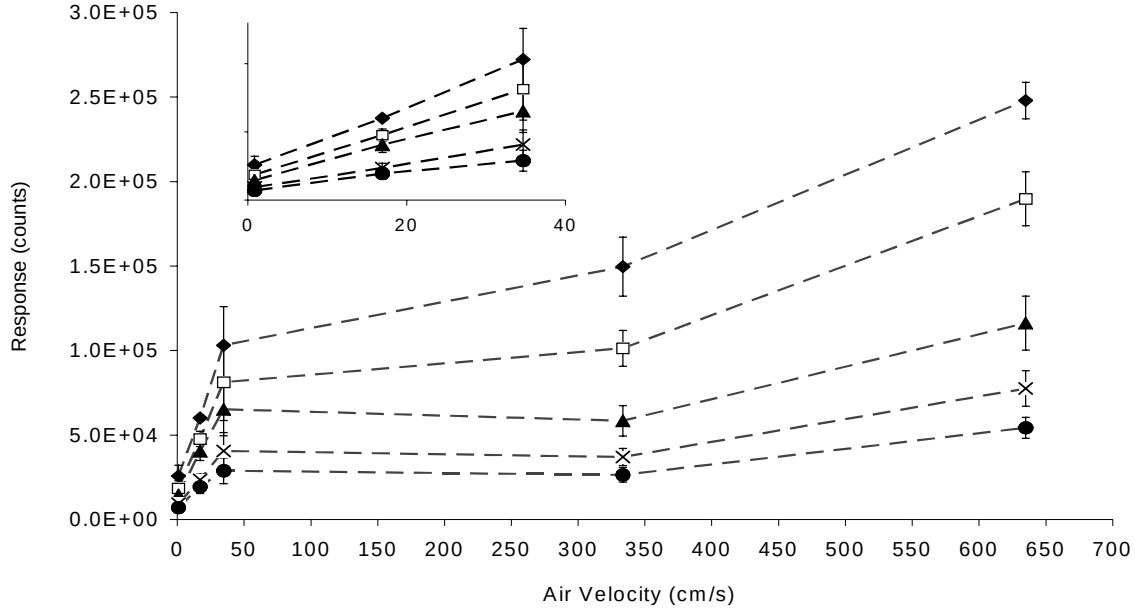


Figure 2-4: Optimum Linear Air Sampling Velocity for HSA-SPME (Ramsey 2006)

The HSA-SPME theory for increased compound uptake is based on four factors: greater polymer volume, more air flow across polymer, a higher polymer surface area-to-air volume ratio, and a reduction in the boundary layer between the polymer and the air. Ramsey *et al* calculated the ratio of polymer surface area to the volume of air in the annular space and determined the HSA-SPME device has nearly a 15-fold greater polymer-to-air ratio than a typical 1 cm SPME fiber (Ramsey 2006). This value was determined by calculating the polymer surface area and air volume inside the annular space and comparing it to a SPME fiber inside a similar volume of air. The HSA-SPME dynamic air sampling design affords high velocity, high volume with some turbulent airflow across the surface of the polymer coating thereby reducing the boundary layer next to the polymer. A thinner boundary layer increases the analyte transfer rate to the

polymer (Ramsey 2006). The volume of polymer on the HSA-SPME device also increases the HSA-SPME capacity.

The HSA-SPME device is physically too large to be directly inserted into a GC/MS injector as with traditional SPME fibers. However, the advantage is that an injector is not required because the polymer coated wire is directly heated. To evaluate the HSA-SPME device, a focusing preconcentrator is used to capture, reconcentrate, and focus the desorbed compounds into the GC/MS. Reconcentration is required due to the large vapor volume generated during the desorption process which creates significant peak broadening in chromatography (Ramsey 2004). However, most field portable GC/MS instruments capable of collecting air samples, have internal preconcentrators compatible with the HSA-SPME desorption technique.

2.3 Field Portable GC/MS

GC/MS is used extensively in laboratory settings and is considered the "gold standard" in identification of VOCs; however, few publications address GC/MS operations in the field. Built with similar, and in some cases identical, laboratory GC/MS components, GC/MS in the field can provide definitive analysis on-site. One study directly compared on-site GC/MS with off-site laboratory GC/MS during cleanup actions at an inactive drum recycling facility and found the results of the two systems very comparable (Schuetz 1995). A field portable GC/MS was used in the Hook *et al* study with the aircraft fire and again in a military painting operation at sea (Hook 2002). Analyses of the painting operation, conducted aboard a Naval ship, were completed within 10 minutes, and results of the aircraft fire were available within 30 minutes. Both

systems identified unknown air contaminates that were later confirmed with laboratory GC/MS. Without field portable GC/MS, these processes would have taken days to complete. The analytical method used in the VX soil contamination study, mentioned previously, was developed on a laboratory GC/MS and successfully implemented in the field with a portable GC/MS system (Hook 2003). In an environmental and forensics application study, several field portable GC/MS systems proved to be very versatile (Eckenrode 2001). One GC/MS unit subjected to rough terrain and a harsh jungle environment characterized VOCs released from an adjacent industrial chemical company. At a CWA demilitarization site, a field portable GC/MS was used to evaluate the performance of the existing detection systems. In the dynamic SPME study of sarin gas, a field portable GC/MS was also used and compared to liquid injection standards (Hook 2003). Sarin was detected at 0.1 mg/m^3 in less than 4 minutes. On-site GC/MS can provide data of high quality with a much faster turnaround time than laboratory analysis, and ensure more effective remediation (or disaster response) efforts with timely, accurate results (Schuetz 1995).

2.4 Low Thermal Mass Resistively Heated GC Column

Due to the increasing need for rapid analysis for emergency response or simply to meet the demand of the ever increasing number of sample requests, resistively heated GC columns have been evaluated as an alternative means to heat columns and achieve shorter overall analysis times. Total analysis time includes both the analysis time and the time the GC/MS instrument needs to cool and reset for the next sample. In 1999, one such device, EZ Flash GC (Thermedics), reduced a 30-minute analysis to about 2.5 minutes

without significant loss of separation efficiency (Dalluge 1999). In this study, a capillary column (5 m X 0.25 mm i.d., film thickness (d_f) = 0.2 μm) was placed inside a metal tube for rapid heating and cooling, and compared to a conventional GC column (23 m X 0.25 mm, d_f = 0.25 μm). The EZ Flash achieved 1200^{o}C/min ramp rates, plus rapid cooling from 300^{o}C to 50^{o}C in 30 seconds. However, the EZ Flash required significant power. In 2001, a study evaluated the prototype LTMGC column (16.2 m x 0.25 mm, d_f = 0.25 μm) (RVM Scientific) against a standard GC column (16.5 m x 0.25 mm, d_f = 0.25 μm) for speed, efficiency, temperature control, resolution, precision, and power demand (Sloan 2001). In this study, the LTMGC column out-performed the standard GC column and traditional oven in both speed and power demand. The total analytical cycle time for the LTMGC was less than 6.2 minutes (120^{o}C/min ramp rate) while the standard column's minimum cycle time was greater than 14 minutes. The aim was to achieve a set resolution for the critical compound pair: cocaine and nortriptyline. The LTMGC column power requirements were 78% less than the traditional oven under equivalent conditions, and the LTMGC's efficiency, resolution, and precision were all comparable to the standard GC column (Sloan 2001). Studies have demonstrated that LTMGC columns significantly decrease the total analytical cycle time and reduce power consumption without sacrificing quality (Dalluge 1999; Sloan 2001; Whitchurch 2003). Dalluge *et al* found, similar to previous studies that separation efficiency decreases significantly with increased temperature ramp rates, but also that this phenomenon could be controlled with increased carrier gas velocities. Dalluge *et al* reaffirmed that there was indeed an optimum linear velocity for each temperature gradient. The LTMGC

presents an equivalent replacement to traditional GC ovens with little impact on current injector systems or detectors.

3 Methodology

This chapter describes the methods used to answer the research question and specific aims identified in Chapter 1. The primary objective of this study was to determine if the HSA-SPME device was capable of rapid, high volume air sampling and evaluate compound extraction across a range of linear velocities through the HSA-SPME device. To do this, known concentrations and volumes of a 39-compound gas mixture were created in Tedlar™ bags and exhausted through the HSA-SPME device using an air sampling pump. The HSA-SPME device was then integrated with a GC/MS instrument, desorbed via resistive heating, and analyzed. Additional HSA-SPME variables such as desorption efficiencies, durability, and longevity were also evaluated. Two types of HSA-SPME devices were evaluated: Carboxen/PDMS and PDMS.

3.1 Compounds Used in the Study

The Environmental Protection Agency (EPA) TO-14 list of 39-compounds (Restek Inc.) was selected for this study. This mixture represents a diverse range of chemical properties (molecular weights, boiling points, etc.) and contains common analytes in environmental sampling and analysis. The molecular weights and boiling points for several of the larger compounds in this mixture offer a good comparison to the molecular weights and boiling points of some of the CWAs, narcotics and explosives. Several of these compounds have been identified as components in both human scent and human decomposition (Curren 2006). Table 3-1 lists the 39-compounds in the EPA TO-14 mixture.

Compound		MW	Boiling Point (^{o}C)	*Density (g/mL)	CAS Number
1	Dichlorodifluoromethane	120.91	-29	1.329	75-71-8
2	Methyl Chloride	50.50	-24	1.780	74-87-3
3	Vinyl Chloride	62.50	-14	2.210	75-01-4
4	Bromomethane	94.95	-16	1.732	74-83-9
5	1,2-dichlorotetrafluoroethane	170.92	3	1.455	76-14-2
6	Ethyl Chloride	64.00	12	0.890	75-00-3
7	Trichlorofluoromethane	137.37	24	1.477	75-69-4
8	1,1-dichloroethene	96.00	31	1.218	75-35-4
9	Methylene Chloride	84.93	40	1.318	75-09-2
10	1,1,2-trichlorotrifluorethane	186.00	48	1.564	76-13-1
11	1,1-dichloroethane	98.96	57	1.168	75-34-3
12	cis-1,2-dichloroethylene	96.94	60	1.265	156-59-2
13	Chloroform	119.38	61	1.480	67-66-3
14	1,2-dichloroethane	98.96	84	1.246	107-06-2
15	1,1,1-trichloroethane	133.40	74	1.330	71-55-6
16	Carbon Tetrachloride	153.82	77	1.583	56-23-5
17	Benzene	78.11	80	0.873	71-43-2
18	1,2-dichloropropane	112.99	96	1.150	78-87-5
19	Trichloroethylene	131.39	87	1.458	79-01-6
20	Cis-1,3-dichloropropene	111.00	104	1.217	10061-01-5
21	Trans-1,3-dichloropropene	110.00	111	1.224	10061-02-6
22	Toluene	92.14	111	0.865	108-88-3
23	1,1,2-trichloroethane	133.40	114	1.435	79-00-5
24	Tetrachloroethylene	165.83	121	1.613	127-18-4
25	1,2-dibromoethane	186.00	131	2.180	106-93-4
26	Chlorobenzene	112.56	132	1.101	108-90-7
27	Ethylbenzene	106.00	136	0.865	100-41-4
28	p-Xylene	106.00	138	0.858	106-42-3
29	m-Xylene	106.17	139	0.861	108-38-3
30	Styrene	104.15	145	0.900	100-42-5
31	o-Xylene	106.17	144	0.876	95-47-6
32	1,1,2,2-tetrachloroethane	167.85	146	1.587	79-34-5
33	1,3,5-trimethylbenzene	120.20	165	0.860	108-67-8
34	1,2,4-trimethylbenzene	120.19	169	0.872	95-63-6
35	m-Dichlorobenzene	146.00	173	1.290	541-73-1
36	p-Dichlorobenzene	147.00	174	1.250	106-46-7
37	o-Dichlorobenzene	147.00	180	1.299	95-50-1
38	1,2,4-trichlorobenzene	181.40	213	1.450	120-82-1
39	Hexachloro-1,3-butadiene	260.70	215	1.550	87-68-3

Table 3-1: Chemical Properties of the 39-Compound Gas Mixture (SAX 1984; NIOSH 1994; CRC 1995) * Density at 25^{o}C

3.2 Analytical Instrumentation

An Agilent laboratory grade GC/MS and Entech 7100 Air Preconcentrator were used to analyze the extracted and desorbed compounds from the HSA-SPME device. The Agilent GC/MS was a Hewlett Packard 6890N GC with a 5973 MS detector. The Agilent had a heated injector port for direct liquid sample injections or SPME fiber insertion. The Agilent's MS used a 70 eV electron impact ionization source to ionize and fragment eluting compounds and a modified Hewlett-Packard monolithic quadrupole mass analyzer. The MS maintained a vacuum pressure of approximately 10^{-5} Torr with a 70 L/sec dual stage turbomolecular/drag vacuum pump. A resistively heated LTMGC column (30 m x 0.25 mm DB-5MS, d_f = 0.25 μm) was attached to the Agilent. In this study, the Agilent's air bath oven was only used as an isothermal transfer line.

The Agilent did not have the capability to directly analyze air samples. Therefore, an Entech 7100 Air Preconcentrator (Entech Instruments) with the capability to collect and concentrate air samples was configured with the Agilent. The Entech was a triple stage concentrator capable of collecting air samples at a rate of 200 mL/min with a maximum sample capacity of 2000 mL. The first stage of the Entech concentrator was a glass bead trap, the second stage was a Tenax™ trap and the third stage was a cold trap focuser. All three stages were cryogenically cooled with liquid nitrogen and the temperature for each stage was independently controlled between –150°C and 190°C.

The concentration process from sample collection to GC/MS transfer is approximately 15 minutes ± 2 minutes depending on sample volumes and transfer rates between traps. Entech Instruments evaluated the Entech 7100 to demonstrate its ability to meet the EPA's stringent air quality standards. The Entech, coupled with a Hewlett

Packard 6890/5973 GC/MS system, achieved limits of detection in the low parts per trillion range (Moezzi 1998). Entech Instruments tested the same 39-compound VOC mixture used in this study.

3.3 Experimental Preparation

3.3.1 Creating Tedlar™ Bag Concentrations

The 1 ppm_v 39-compound gas mixture was diluted to specific concentrations using a precision gas standard generator (Kin-tek Laborartories), nitrogen gas (Airgas, 99.99% pure), and Tedlar™ bags (SKC). The 39-compound gas mixture was diluted 1:99 with nitrogen through the Kin-tek to create a 10 ppb_v concentration. The Kin-tek mixed the two gases simultaneously. Tedlar™ bags were triple purged with nitrogen and then triple purged with the desired sample concentration to minimize potential losses to the Tedlar™ bags. The dilution flow rates from the gas generator for both gases were verified with an ADM3000 Intelligent Digital Flow meter.

3.3.2 Calibrating Air Sampling Pumps

Two Gilian air sampling pumps were used to exhaust the Tedlar™ bags through the HSA-SPME. A low flow GilAir5 personal air sampling pump was used to sample with flow rates less than 5 L/min and a Gilian high flow area sampler was used to sample flow rates greater than 5 L/min. The Gilian air sampling pumps were calibrated daily using a DC-Lite Primary Flow Meter (Bios) with an average of 10 measurements.

Dividing the pump flow rates by the cross-sectional area of the HSA-SPME device allows calculation of the linear velocity through the HSA-SPME. The cross-sectional

area is calculated using Equation 3-1. The inside radius of the outer glass tube is 1.5 mm and the outside radius of the inner glass tube is 0.6 mm. The cross sectional area of the annular space is calculated to be 0.0594 cm^2. The conversion from flow rates to linear velocity is calculated using Equation 3-2. Table 3-2 displays the flow rates used in this study with their equivalent linear velocities. The table also displays the linear velocity in miles per hour (mph) for better understanding of the speed of airflow through the HSA-SPME device.

Cross Sectional Area of Annular Space = $\pi * r^2_{(outer)} - \pi * r^2_{(inner)}$ **Eq. 3-1**

$$= \pi (1.5 \text{ mm})^2 - \pi (0.6 \text{ mm})^2 = 5.94 \text{ mm}^2 = 0.0594 \text{ cm}^2$$

Sample conversion from 0.1 L/min to linear velocity in cm/sec

$$\frac{0.1 \text{ L/min} * 1 \text{ min/60 sec} * 10^3 \text{ cm}^3/\text{L}}{0.0594 \text{ cm}^2} = 28 \frac{\text{cm}}{\text{sec}}$$ **Eq. 3-2**

Flow Rate (L/min)	Linear Velocity (cm/sec)	Linear Velocity (mph)
0.1	28	0.6
0.5	140	3
1.5	421	9
3	842	19
5	1403	31
10	2807	63

Table 3-2: Air Sampling Flow Rates and Linear Velocities Through the HSA-SPME Device

3.3.3 Analytical Instrumentation Preparation

The Agilent and Entech were prepared for analysis daily. The Agilent's injector, transfer lines, and oven were heated to 200^{o}C, and the MS transfer line to 215^{o}C for 30-minutes. The carrier gas pressure was set at 20 psi. The Agilent was then tuned with perfluorotributylamine (PFTBA) using the Chemstation software Standard Spectra tune. The Entech traps were heated to 190^{o}C for 15 min to remove any residual compounds. A blank analysis was accomplished each day prior to any experimental sample analysis.

3.3.4 HSA-SPME Device Conditioning

The HSA-SPME devices used in this research were new prototype devices that required conditioning to avoid loose polymer debris from being introduced into the analytical instrumentation. The HSA-SPME devices were conditioned at approximately 250^{o}C for 30 minutes with a constant flow of helium (80 – 100 mL/min) through the device. A 10 watt, 10 ohm resistor was placed in-line with the 24V circuit switch power supply and the HSA-SPME device. The resistor held the polymer temperature at or below the recommended conditioning temperatures established for conventional SPME fibers of similar coatings and thickness.

3.4 Specific Aim #1: Develop Method for HSA-SPME and GC/MS

The first aim was to create a comprehensive analytical method for the combination of the Agilent GC/MS, LTMGC column, and the Entech, as well as the integration of the HSA-SPME device. In order to calibrate the system without the influence of the HSA-SPME device, a 50 ppb_v concentration of the 39 compounds was introduced to the Entech and analyzed on the Agilent with a LTMGC column. The mixture was prepared in a 1 L Tedlar™ bag using the method described in section 3.3.1 with a nitrogen dilution of 1:4. The parameters of the instruments were manipulated to minimize analytical speed while maintaining quality peak resolution for the 39 compounds.

Next, the analytical method developed with the direct Tedlar™ bags was used with the HSA-SPME devices. The HSA-SPME devices were exposed to the same 39 compounds in the Tedlar™ bags and desorbed into the Entech. To desorb the HSA-SPME device into the Entech, the nickel alloy wire was resistively heated with the 24V circuit switch. The use of an in-line resistor slowed the desorption process to nearly two minutes, which was counterproductive to rapid detection (Ramsey 2004); therefore, the in-line resistor was not used. However, without the in-line resistor, this resistive heating system was capable of temperature ramp rates in excess of 4000^{o}C/min, which could potentially damage the polymer material (Mustacich 2003). Therefore, the optimum desorption time for the HSA-SPME device without damaging the polymer was important to determine. Helium carrier gas was used through the HSA-SPME device during the desorption process to avoid the potential risk of damage to the polymer due to the presence of oxygen (Ramsey 2004).

To determine the optimal desorption time for the HSA-SPME devices, two HSA-SPME devices were tested: 30 μm Carboxen/PDMS and 30 μm PDMS. The HSA-SPME devices were attached to 1 L Tedlar™ bags, which contained the 39 compounds at a concentration of 50 ppb_v. The other end of the HSA-SPME devices were attached to a GilAir5 personal air sampling pump calibrated to 1 L/min, as described in section 3.3.2. Connections were made with small lengths of Tygon tubing. The air sampling pump was then turned on and the entire 1 L sample was passed through the HSA-SPME devices.

After sampling, the HSA-SPME devices were then disconnected from the bag and pump, and promptly connected to the Entech Agilent system. A 3 L Tedlar™ bag filled with helium was attached to the back end of the HSA-SPME devices so helium would flow through the HSA-SPME device during the desorption process. Again, Tygon tubing was used for the connections. The Entech's internal air sampling pump was set to a flow rate of 200 mL/min for 2.5 min. A sampling time of 2.5 min was used to ensure oxygen was removed from the HSA-SPME devices and to make certain desorbed compounds reached the concentrator traps and were not left in the sampling line. The sampling line was approximately 1 meter in length. Fifteen seconds into the desorption process, the HSA-SPME device was resistively heated at 2, 3, 4, 5 and 6 second lengths of time and analyzed to maximize the desorption efficiency without damaging the polymer. These times were selected because in the previous study damage was noted at desorption intervals greater than 5 – 7 seconds (Ramsey 2004).

Following the initial desorption and analysis, the HSA-SPME device was sequentially desorbed and analyzed an additional three times to determine how much of the 39 compounds remained on the polymer. Not all compounds are fully desorbed during the

initial desorption. Equation 3-3 was used to calculate the initial desorption efficiency at each time interval for each compound. The desorption efficiency for each of the 39 compounds was determined from the peak areas of the initial desorption, divided by the sum the peak areas of all four desorptions for each compound. As the desorption time increases, more compound may be desorbed from the polymer, but the polymer may also become damaged because of the rapid temperature increase. The HSA-SPME devices were evaluated for visible signs of polymer damage or deterioration under a microscope following each desorption time interval.

$$\text{Desorption Efficiency}\,(\%) = \left(\frac{\text{Peak Area From Initial Desorption}}{\text{Peak Area From All Desorptions}}\right) * 100 \qquad \textbf{Eq. 3-3}$$

Example: Initial Desorption Peak Area: 7,500 units
2^{nd} Desorption Peak Area: 1,500 units
3^{rd} Desorption Peak Area: 1,000 units
4^{th} Desorption Peak Area: 0 units

$$\text{Desorption Efficiency} = \frac{7500}{7500 + 1500 + 1000 + 0} * 100 = 75\%$$

In this scenario, 75% of this compound was desorbed during the initial desorption.

3.5 Specific Aim #2: Measure extraction efficiency for six velocities through the HSA-SPME device

Extraction efficiency is the total amount of a compound extracted by the HSA-SPME device from the sampling environment (air or water) and introduced into the GC/MS. The goal is to maximize the total extraction. With higher velocity flowing through the HSA-SPME device, the boundary layer where a compound transfers from the air to the polymer is reduced, potentially

increasing extraction. However, a competing factor in compound transfer is total contact time between the compound and the polymer, which may likely reduce extraction. The purpose of measuring the extraction efficiency is to see if there is enough efficiency at the higher velocities to increase the total mass of analyte introduced to the CG/MS and ultimately support rapid, high volume trace level sampling.

Six velocities were tested: 28, 140, 421, 842, 1403, and 2807 cm/sec; as shown in Table 3-3. These six velocities were selected to expand upon previous work performed at 20 to 800 cm/sec with the same compounds (Ramsey 2006). For simplistic terminology, these linear velocities will be referred to in terms of air sampling flow rates.

Extraction efficiency at each flow rate was determined by dividing the peak area of each compound from the HSA-SPME device by the peak area of the same compound at the same concentration analyzed directly from the 1 L Tedlar™ bag. Results from direct analysis of the 1 L Tedlar™ bag was assumed 100% extraction. Because 1 L Tedlar™ bags at 10 ppb_v were used for all six flow rates, the same mass of each compound was passed through the HSA-SPME device in each experiment. It is expected that the HSA-SPME device will not be able to collect all the compounds in the 1 L Tedlar™ bag so compound peak areas with the HSA-SPME device should always be less than the peak areas directly from the 1 L Tedlar™ bag. An example demonstrating the extraction efficiency calculations is shown with Equation 3-4.

$$\text{Extraction Efficiency}\,(\%) = \left(\frac{\text{Total Peak Area From Four Desorptions}}{\text{Peak Area From Direct Bag Analysis}}\right) * 100 \qquad \textbf{Eq. 3-4}$$

Example: Initial Desorption Peak Area: 7500 units
2^{nd} Desorption Peak Area: 1500 units

3rd Desorption Peak Area:	1000 units
4th Desorption Peak Area:	0 units
Direct Analysis from Bag Peak Area:	100,000 units

$$\text{Extraction Efficiency} = \left(\frac{7500 + 1000 + 1000 + 0}{100{,}000} \right) * 100 \quad = \quad 10\%$$

In this scenario, the extraction efficiency for that compound at that specific flow rate was 10%.

The experiment began by sampling a 1 L Tedlar™ bag with a concentration of 10 ppb_v of the 39 compounds at a flow rate of 0.1 L/min. Tedlar™ bag mixtures, calibrations and fiber conditioning procedures were as described in section 3.3. Two new HSA-SPME devices were used for this aim: 15 μm Carboxen/PDMS and 65 μm PDMS. The Tedlar™ bag was entirely exhausted through the HSA-SPME device and then promptly connected to the Entech Agilent system for analysis. The HSA-SPME device was desorbed a total of four times, with GC/MS analysis for each desorption, to ensure 100% of the compounds were desorbed. The sum of the four desorptions for each compound was assumed to represent the total mass of the compounds extracted. Each flow rate was evaluated and then the next higher flow rate was measured in ascending order. Each set of six flow rates was repeated a total of three times. Flow rates were measured in this order to reduce the influence of polymer degradation throughout the experiment due to the number of desorptions. Degradation of the HSA-SPME device was expected. Commercial SPME fibers can achieve 50 – 100 desorptions before significant degradation is experienced.

3.6 Specific Aim #3: Compare Total Compound extraction at 0.1 and 10 L/min For a 10 Second Sample at 10 ppb_v for 39 Compounds

This aim was designed to fix sampling time to 10 seconds and compare total compound extraction at the highest and lowest flow rates with the HSA-SPME device. Extraction efficiencies from specific aim #2 were based on reduced boundary layer and compound-polymer contact time; now the total volume delivered to the HSA-SPME device was increased. A 10 L Tedlar^{TM} bag at 10 ppb_v was filled with enough volume to collect samples from the same bag to minimize potential errors introduced from multiple sample bags. Each flow rate was evaluated three times. Again, method procedures were performed as described in the previous sections. A new 30 μm Carboxen/PDMS HSA-SPME device was used.

3.7 Specific Aim #4: HSA-SPME Device Longevity and Durability

The final aim of this study was to characterize the HSA-SPME device as a potential field sampling tool. The parameters noted included HSA-SPME device longevity and durability. No additional procedures or method steps were conducted unique to this aim. Data gathered or observations perceived were documented as useful information for follow-up studies. Longevity and durability were based on perception. Information for both PDMS and Carboxen/PDMS HSA-SPME devices were documented.

4 Results

4.1 Analytical Instrumentation Method Development

4.1.1 GC/MS, LTMGC, and Entech

The first aim of this research was to create a single analytical method for the concentration and analysis of the 39 compounds for the Entech Agilent system. Rapid analytical speed while maintaining peak resolution was the primary objective. Figure 4-1 displays the 39-compound chromatogram produced by the Entech Agilent system. Table 3-1 correlates the numbers in Figure 4-1 to the compound names. The Entech concentrator took 15 ± 2 min but no attempt was made to reduce the time on the Entech concentrator. Temperatures and bake times were increased to ensure no residual compounds remained in the Entech. The Agilent GC/MS analysis time, with the LTMGC, was reduced from 25.5 minutes to 15 minutes. Tables 4-1 and 4-2 show the initial and the modified method parameters selected for the remainder of the study. The Agilent operated in splitless mode with an ion scan range of 50 – 350 *m/z*.

The full temperature ramping capability of the LTMGC could not be used as it caused coelution with poorly defined peak shape between some of the compounds. A temperature ramping rate of only 15^{o}C/min was used for the 39 compounds in this study because of coelution problems. However, the LTMGC was cooled from 200^{o}C and reset to 35^{o}C in less than 4 minutes, much faster than traditional GC air bath ovens. Preliminary testing with a diverse mix of 17 CWA simulants and a combination of ramping rates up to 120^{o}C/min, reduced the GC/MS analytical time from 25 minutes to less than 5 minutes.

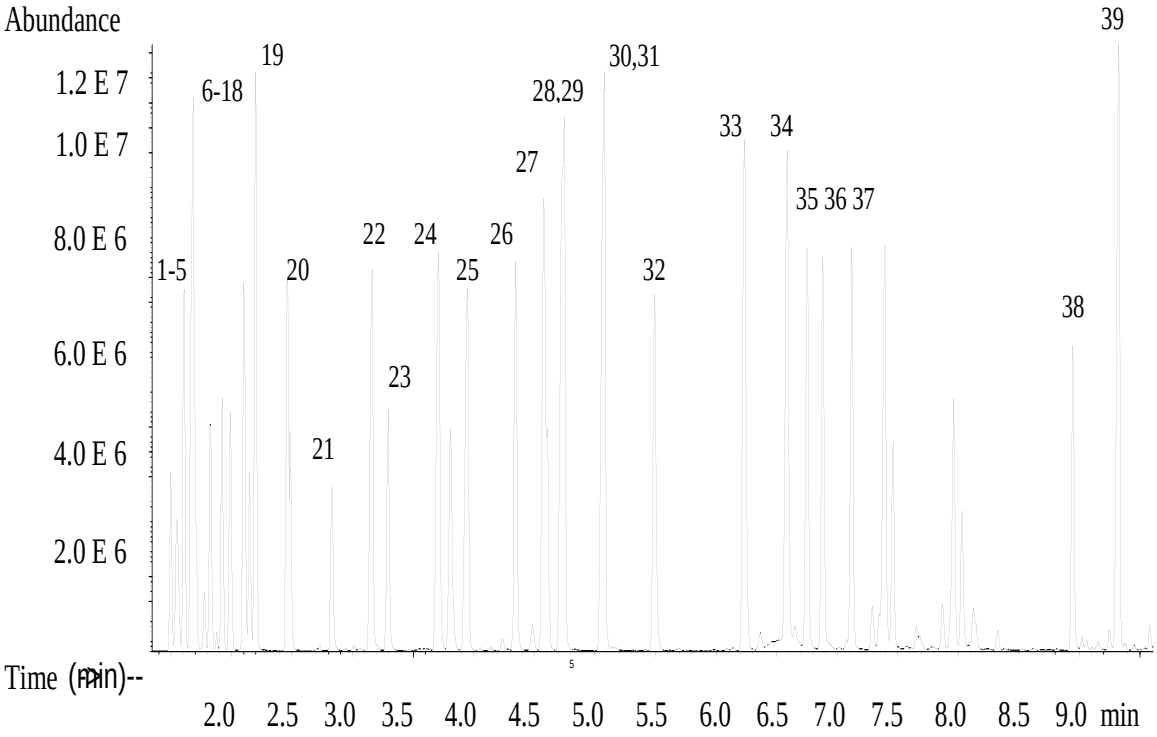


Figure 4-1: Chromatography for a 1 L 50 ppb_v (nominal) Sample of the 39 Compounds Directly Sampled and Analyzed by the Entech, Agilent and LTMGC

Entech 7100 Preconcentrator			
Component		**Initial Method**	**Modified Method**
Inlet Line:		80°C	120°C
Internal Valve		100°C	150°C
Transfer Line		100°C	150°C
Module #1	Trap	-150°C	-150°C
	Preheat	20°C	50°C
	Desorb	30°C	70°C
	Bake	70°C	180°C
Module #2	Trap	-50°C	-50°C
	Preheat	160°C	160°C
	Desorb	180°C	180°C
	Bake	190°C	190°C
Module #3	Trap	-160°C	-160°C
	Desorb	100°C	130°C
	Transfer Time	2 min	2 min
	Total Time:	**15 min ± 2**	**15 min ± 2**

Table 4-1: Initial and Modified Method for the Entech 7100 Preconcentrator

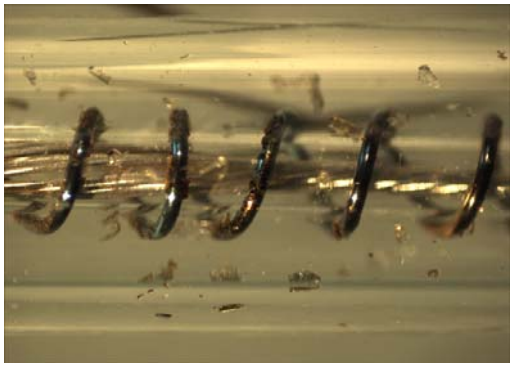
Agilent GC/MS		
Component	**Initial Method**	**Modified Method**
Injector Temp	250°C	200°C
Injector Transfer Line	250°C	200°C
Oven	250°C	200°C
MS Transfer Line	265°C	215°C
Column Head Pressure	10 psi	20 psi
LTMGC Column		
Component	**Initial Method**	**Modified Method**
Starting Temp	35°C (2 min hold)	35°C (2 min hold)
Ramp Rate	10°C/min	15°C/min
Final Temp	250°C (2 min hold)	200°C (2 min hold)
Total Time:	**25.5 min**	**15 min**

Table 4-2: Initial and Final Parameters for the Agilent GC/MS and LTMGC Column

4.1.2 Integration of the HSA-SPME Device with Analytical Instrumentation

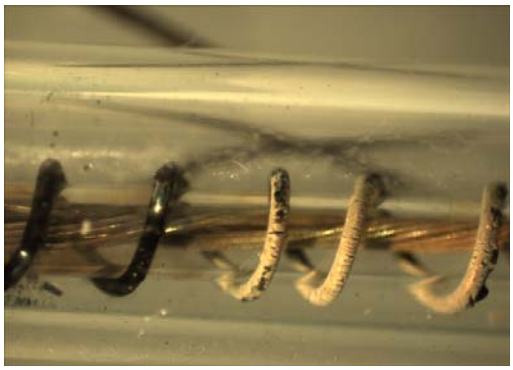
Resistive heat desorption of the HSA-SPME device proved difficult to manage with the 24V manual circuit switch. The actual maximum temperature reached by the HSA-SPME devices could not be measured or controlled with the switch. The desorption time experiment tested intervals between 2 – 6 seconds and the results indicated that continuous desorption intervals greater than 2-seconds caused significant damage to the HSA-SPME device. Figure 4-2 displays progressive changes in the HSA-SPME polymers due to prolonged (greater than 2-seconds) desorption. The upper row of pictures shows unused PDMS and Carboxen/PDMS HSA-SPME devices. The middle row shows a slow progression of white discoloration from just a few desorptions at 5 – 6 second intervals, and the bottom row shows complete discoloration, cracking and flaking of the polymer due to more than 25 desorptions using time intervals greater than 2-seconds. White discoloration, cracking, and flaking of the polymer are signs of a damaged HSA-SPME. The devices in the last row were no longer effective at extracting compounds and were discarded.

PDMS HSA-SPME Device - New



Carboxen/PDMS HSA-SPME Device - New

PDMS With Discoloration and Cracking



Carboxen/PDMS With 50% Discoloration

PDMS After 25 Desorptions (>2 sec)

Carboxen/PDMS After 25 Desorptions (>2 sec)

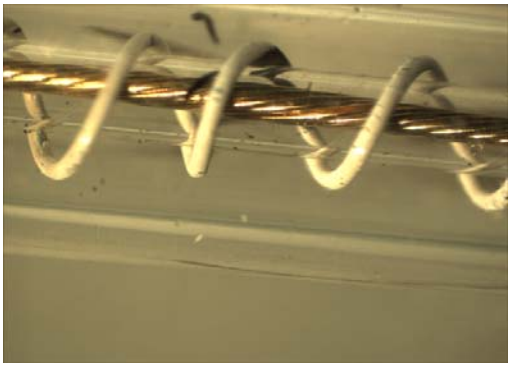


Figure 4-2: Visual Appearance of 30 µm PDMS and 30 µm Carboxen/PDMS HSA-SPME Devices With Cumulative Damage Due to Desorption Times Greater Than 2-Seconds

Desorption times longer than 2-seconds, did not appear to damage the HSA-SPME device immediately. However, signs of damaging temperatures, such as a glowing red wire and smoke, appeared after just a few desorption cycles when desorption times greater than 2-seconds were used. Polymer coatings will eventually degrade with continued desorptions; however, desorption times longer than 2-seconds damaged the HSA-SPME device much faster. Using a 2-second desorption time, the HSA-SPME polymer coatings were effective at extracting compounds up to approximately 80 desorptions.

The 2-second desorption time interval not only prolonged the usefulness of the HSA-SPME device, it also proved sufficient for desorbing the compounds from the Carboxen/PDMS HSA-SPME device. The Carboxen/PDMS HSA-SPME device achieved an average initial desorption efficiency of 93% throughout the entire study. Following the second desorption, the Carboxen/PDMS reached 99% for a majority of the compounds. In contrast, the initial desorption for the PDMS HSA-SPME device, resulted in an average of only 54% desorption efficiency. The PDMS desorption efficiency data is taken from four samples drawn at a flow rate of 0.1 L/min, because the PDMS polymer failed at high sample velocities. Table 4-3 lists the desorption efficiencies, for each of the compounds using a 2-second desorption interval. The reduced desorption efficiency for the PDMS is partly due to the absorptive characteristics of PDMS polymers. PDMS absorbs compounds into the polymer, where as Carboxen adsorbs compounds on the surface. Absorbed compounds require additional energy (increased heat and/or longer heat times) to improve desorption.

Compound	65 μm PDMS	15 μm Carboxen/PDMS
1,2-dichlorotetrafluoroethane	39	58
Vinyl Chloride	18	100
Bromomethane	38	100
Ethyl Chloride	24	56
Trichlorofluoromethane	21	62
1,1-dichloroethene	39	94
Methylene Chloride	45	47

Table 4-3: Percent Desorption Efficiency 65 µm PDMS and 15 µm Carboxen/PDMS HSA-SPME Devices (Initial Desorption)

The results of the 15 µm Carboxen/PDMS desorption efficiency for the lowest (0.1 L/min) and highest (10 L/min) flow rates are shown in Figures 4-3 and 4-4, respectively. The lowest (white) bar of the stacked columns represents the initial desorption. The percentage desorbed from the second, third, and fourth desorptions cycles are represented by the dark, then white then dark bands at the top of the stacked columns. Figures 4-3 and 4-4 clearly show that the majority of the compounds are desorbed in the initial desorption cycle. All four bars together represent the total percentage of compounds extracted from the air and delivered to the Entech Agilent system. Appendix B contains the figures for the remaining flow rates.

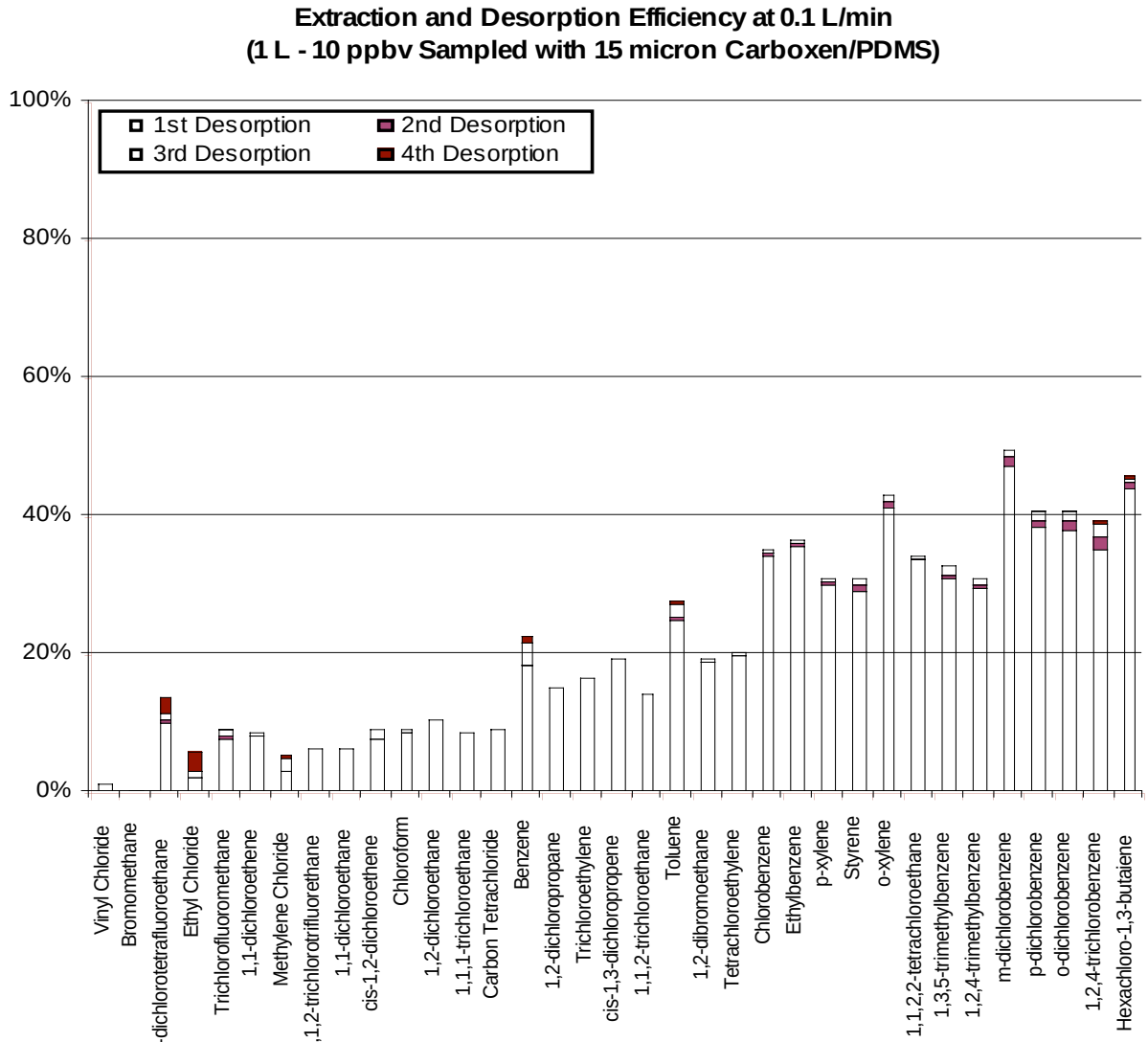


Figure 4-3: Extraction and Desorption Efficiencies For VOCs at a Flow Rate of 0.1 L/min

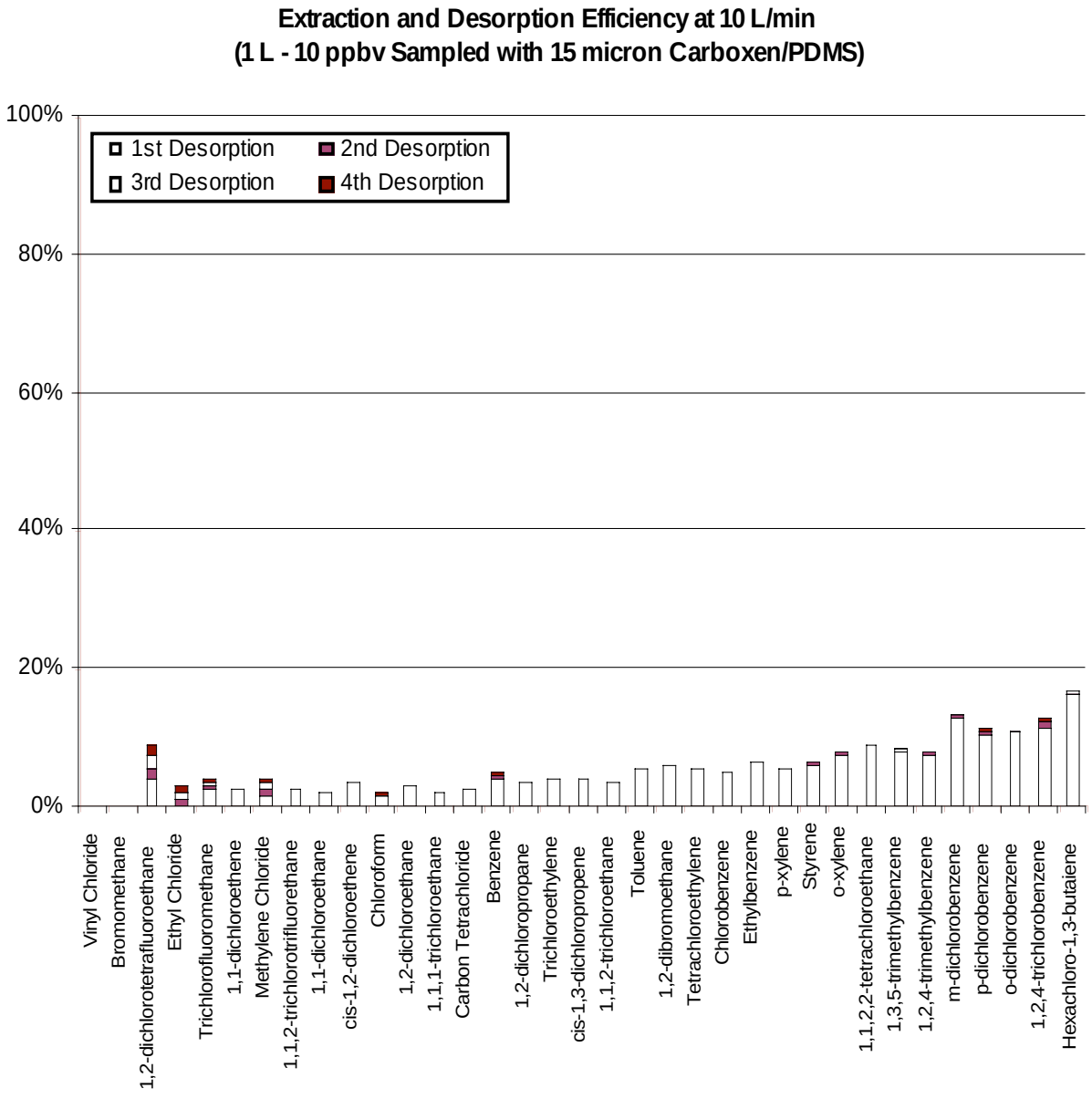


Figure 4-4: Extraction Efficiencies For VOCs at a Flow Rate of 10 L/min

4.2 Extraction efficiency for the six velocities through the two HSA-SPME devices

4.2.1 PDMS HSA-SPME Device

Of the two polymer types, the 65 µm PDMS HSA-SPME devices could not continue to be tested because at 1.5 L/min, the polymer coating was stripped from the nickel alloy wire while collecting samples at ambient temperatures. The initial inspection

of the 65 µm PDMS HSA-SPME devices showed non-uniform polymer coating along the nickel alloy wire, possibly due to the manual winding technique around the inner tube. This irregular polymer coating caused polymer material to protrude into the annular space. The higher velocities through the HSA-SPME device tore the polymer coating from the wire. This problem was repeated with two 65 µm PDMS HSA-SPME devices. The first PDMS HSA-SPME device lost its polymer coating at a flow rate of 10 L/min while the second device lost its coating at 1.5 L/min. Figure 4-5 shows a side-by-side comparison of an unused 65 µm PDMS HSA-SPME device (left) and the 65 µm PDMS HSA-SPME device (right) just after sampling with a flow rate of 1.5 L/min. The rest of this study was performed with the Carboxen/PDMS HSA-SPME devices only.

65 µm PDMS Before 1.5 L/min Sample **65 µm PDMS After 1.5 L/min Sample**

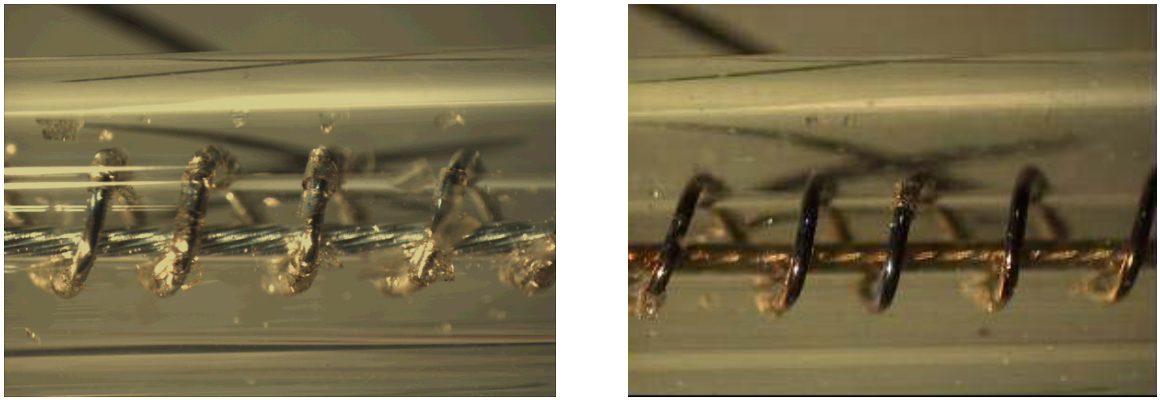


Figure 4-5: 65 µm PDMS HSA-SPME Device Before (Left) and After (Right) Sampling at a Flow Rate of 1.5 L/min.

4.2.2 Carboxen/PDMS HSA-SPME Device

The polymer coating of the 15 µm Carboxen/PDMS HSA-SPME device is able to tolerate flow rates up to 10 L/min. Unlike the PDMS polymer coating, initial evaluation of the Carboxen/PDMS polymer coating shows a smooth coating that appeared to have a

uniform thickness. The extraction efficiency results for the flow rates are displayed in Figures 4-6. The data represent an average of three 1 L Tedlar™ bag samples, containing 10 ppb_v of all 39 compounds. The extraction efficiency is the percentage extracted by the HSA-SPME device from the 1 L Tedlar™ bag and introduced into the Entech Agilent system. Only the 0.1, 5 and 10 L/min flow rates are displayed for the sake of clarity, but efficiency results for all six flow rates can be found in appendix A.

The results for the 15 μm Carboxen/PDMS HSA-SPME device display a decrease in extraction efficiency as flow rate increases. The highest extraction efficiency for nearly all the compounds was achieved with a flow rate of 0.1 L/min. The higher extraction efficiencies at the lower flow rates are likely due to the increased compound-polymer contact time. At 0.1 L/min, the compounds have 100 times the contact time with the polymer coating than at 10 L/min. The 0.1 L/min flow rate required a sampling time of 10 min to exhaust the entire 1 L sample, where as the 1 L sample was exhausted in only 6 sec at 10 L/min.

The 15 μm Carboxen/PDMS HSA-SPME extracted 37 of the 39 compounds missing dichlorodifluoromethane and methyl chloride, and displayed inconsistent results for vinyl chloride, bromomethane, 1,2-dichlorotetrafluoroethane, and ethyl chloride. It was expected that the 15 μm Carboxen/PDMS HSA-SPME device would not trap dichlorodifluoromethane and methyl chloride due to their very low boiling points of -29^{o}C and -12^{o}C, respectively.

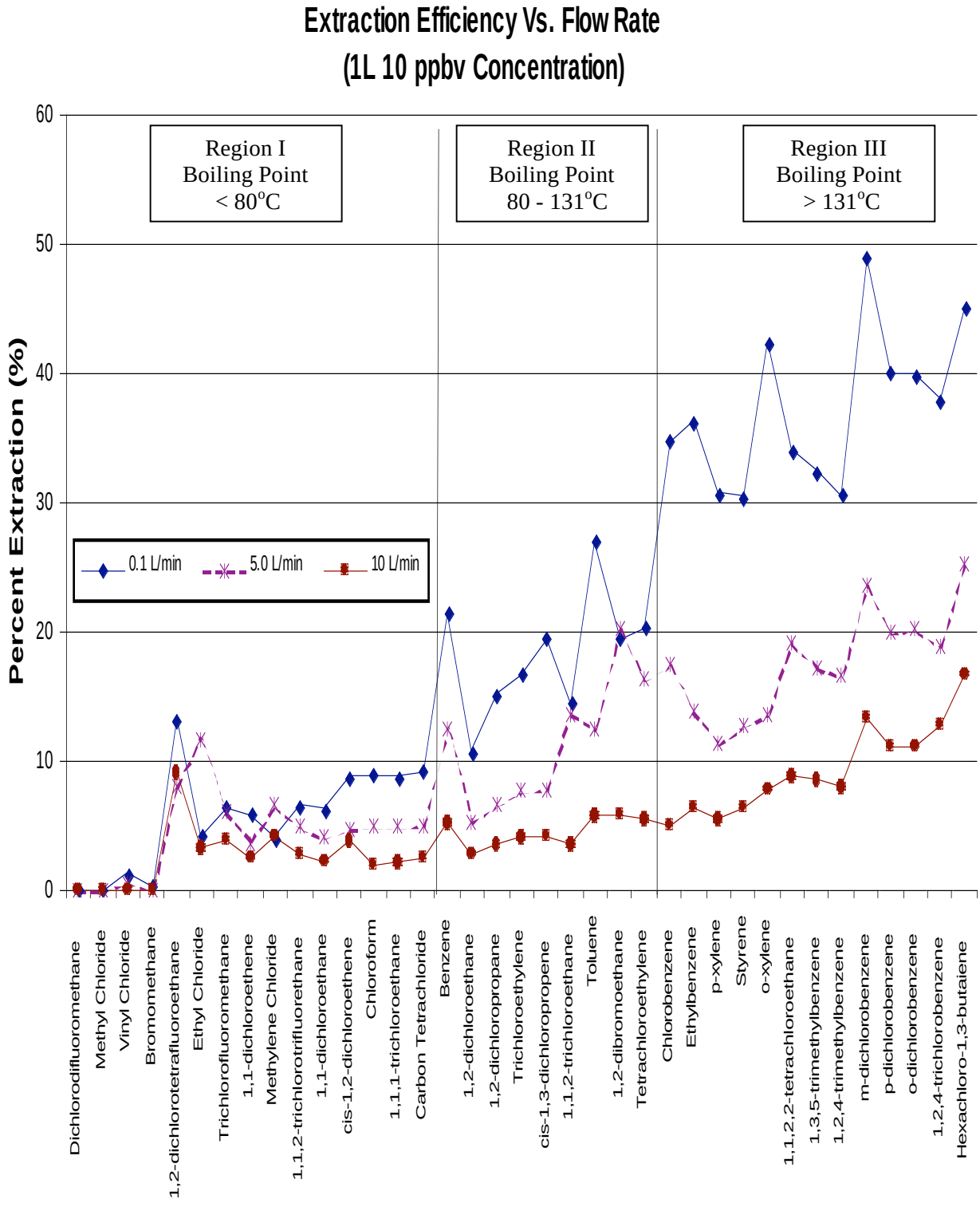


Figure 4-6: Extraction Efficiency For a 15 µm Carboxen/PDMS HSA-SPME Device at 0.1, 5 and 10 L/min Flow Rates

Molecular weight and boiling point are two common chemical properties that typically affect compound extract by SPME polymers. Visual observation of the molecular weight compared to extraction efficiency did not show that molecular weight had any influence on extraction efficiency. However, boiling point, proved to be a good predictor of compound extraction. Figure 4-6 was divided into three regions based on boiling point ranges. Table 4-4 lists the 39 compounds in each region with their boiling points. In Figure 4-6, it can be seen that the compounds with the highest boiling point, had the highest extraction efficiency. The compounds with a high boiling point were more easily captured by the Carboxen/PDMS HSA-SPME device. The compounds with low boiling points were likely too volatile to remain absorbed onto the polymer.

Compound Grouping Based on Boiling Point					
Region I Boiling Points < 80°C		**Region II Boiling Points 80-131°C**		**Region III Boiling Points > 131°C**	
Dichlorodifluoromethane*	-29	Benzene	80	Chlorobenzene	132
Methyl Chloride*	-12	1,2-dichloroethane	84	Ethylbenzene	136
Vinyl Chloride**	-14	1,2-dichloropropane	96	m-Xylene	139
Bromomethane**	-16	Trichloroethylene	87	p-Xylene	138
1,2-dichlorotetrafluoroethane	3	Cis-1,3dichloropropene	104	Styrene	145
Ethyl Chloride**	12	Trans-dichloropropene	111	o-Xylene	144
Trichlorofluoromethane	24	Toluene	111	1,1,2,2-tetrachloroethane	146
1,1-dichloroethene	31	1,1,2-trichloroethane	114	1,3,5-trimethylbenzene	165
Methylene Chloride	40	Tetrachloroethylene	121	1,2,4-trimethylbenzene	169
1,1,2-trichlorotrifluorethane	48	1,2-dibromoethane	131	m-Dichlorobenzene	173
1,1-dichloroethane	57			p-Dichlorobenzene	174
cis-1,2-dichloroethylene	60			o-Dichlorobenzene	180
Chloroform	61			1,2,4-trichlorobenzene	213
1,1,1-trichloroethane	74			Hexachloro-1,3-butadiene	215
Carbon Tetrachloride	77				

Table 4-4: Compound Grouping Based on Boiling Point

* Compounds were not extracted by the Carboxen/PDMS HSA-SPME device.

** Compounds were not consistently detected in all three samples.

4.3 Compare compound uptake at highest and lowest linear velocities

Despite the lower extraction efficiency illustrated in Figures 4-6, when sample time was held constant, the 10 L/min flow rate was able to extract more compound mass than the 0.1 L/min flow rate. In Figure 4-7, sampling time was held constant at 10 seconds and a concentration of 10 ppb_v was used for all 39 compounds. The highest flow rate (10 L/min) and lowest (0.1 L/min) flow rates are compared. Figure 4-7 reveals that the higher flow rate of 10 L/min ultimately collects the highest total mass of compounds over the lower flow rate of 0.1 L/min.

Across the range of compounds, there is an average 8-fold increase in compound extraction at the higher flow rate. The data points represent an average of three replicates. Table 4-5 lists the average total extraction and relative standard deviation (RSD) at both flow rates for the 39 compounds, as well as the increase in total compound extraction.

4.4 Longevity and Durability of HSA-SPME Device

Other parameters that were noted during this study included longevity and durability of the HSA-SPME device. Longevity and durability of the HSA-SPME devices were qualitatively assessed throughout the study. Longevity was identified as how long the HSA-SPME device could effectively extract compounds from the environment. With a 2-second desorption, the 15 μm Carboxen/PDMS HSA-SPME device continued to be effective at extracting compounds beyond 80 desorptions. The polymer coating

was beginning to show signs of damage at this point with white discoloration. Beyond 80 desorptions, the HSA-SPME device degradation became more progressive with each additional desorption.

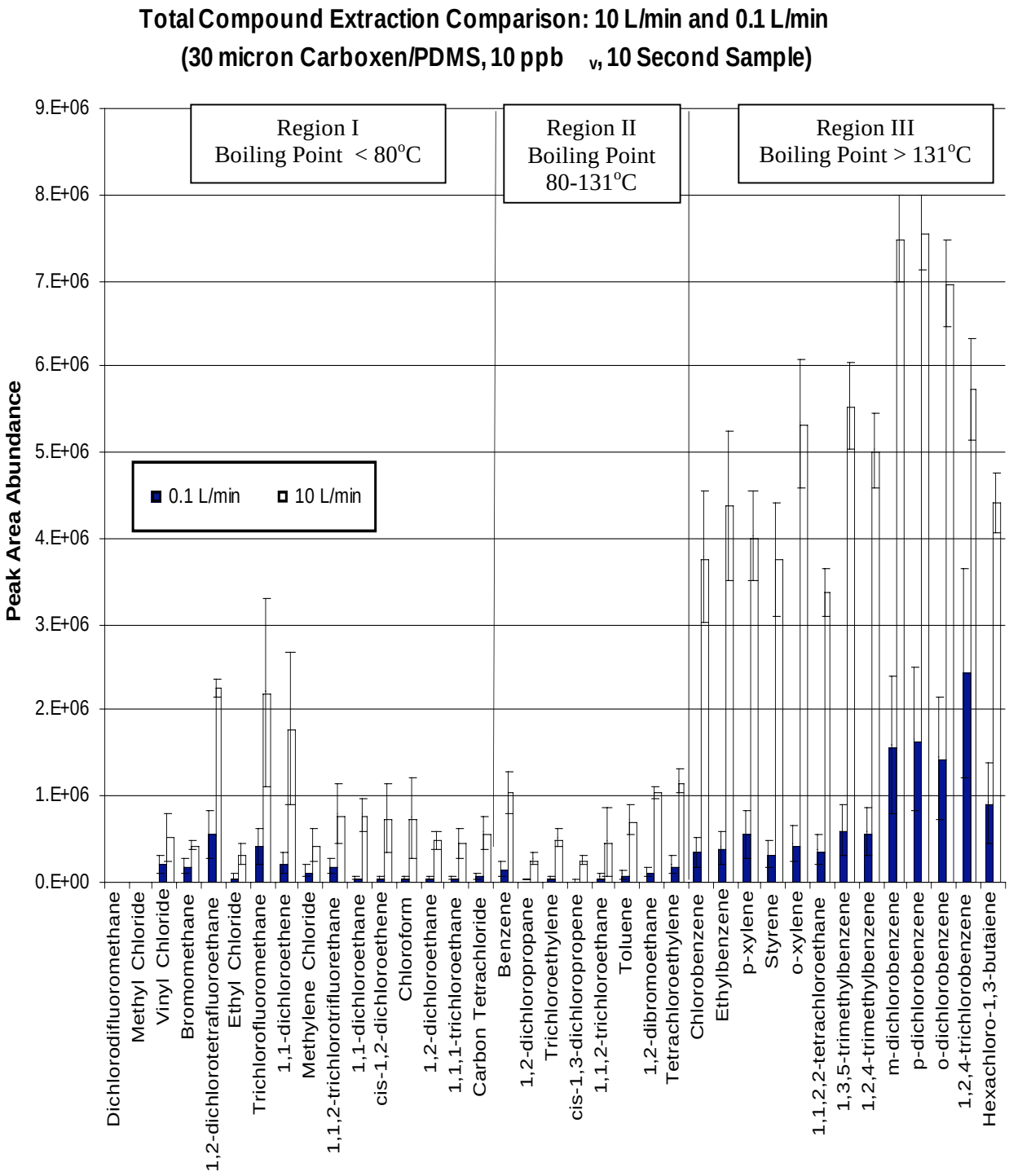


Figure 4-7: Direct Comparison of 0.1 and 10 L/min Using a 10-second Sampling Time and 30 µm Carboxen/PDMS HSA-SPME Device

Compound	Total Extraction 0.1 L/min	RSD	Total Extraction 10 L/min	RSD	Extraction Ratio 10 vs 0.1 L/min
Vinyl Chloride	212,636	1	528,014	53	2.5
Bromomethane	178,553	8	421,576	11	2.4
1,2-dichlorotetrafluoroethane	554,046	1	2,254,868	4	4.1
Ethyl Chloride	52,723	27	336,099	35	6.4
Trichlorofluoromethane	416,654	23	2,207,446	50	5.3
1,1-dichloroethene	224,019	2	1,776,795	50	7.9
Methylene Chloride	125,025	24	416,008	47	3.3
1,1,2-trichlorotrifluorethane	172,310	NA	784,931	46	4.6
1,1-dichloroethane	51,961	32	776,052	25	14.9
cis-1,2-dichloroethene	48,237	NA	738,225	53	15.3
Chloroform	48,341	3	745,733	63	15.4
1,2-dichloroethane	35,679	16	484,113	22	13.6
1,1,1-trichloroethane	43,833	17	450,044	38	10.3
Benzene	71,910	39	570,080	34	7.9
Carbon Tetrachloride	145,252	17	1,037,720	25	7.1
1,2-dichloropropane	17,435	NA	267,495	22	15.3
Trichloroethylene	49,439	11	506,306	23	10.2
cis-1,3-dichloropropene	16,671	17	252,534	20	15.1
1,1,2-trichloroethane	58,872	11	464,504	86	7.9
Toluene	82,154	29	710,782	24	8.7
1,2-dibromoethane	111,312	43	1,041,105	8	9.4
Tetrachloroethylene	192,930	53	1,173,767	12	6.1
Chlorobenzene	350,923	33	3,786,229	20	10.8
Ethylbenzene	392,652	36	4,378,724	20	11.2
p-xylene	550,702	60	4,027,366	13	7.3
Styrene	321,142	20	3,755,464	18	11.7
o-xylene	443,615	20	5,337,636	14	12.0
1,1,2,2-tetrachloroethane	372,250	13	3,378,333	8	9.1
1,3,5-trimethylbenzene	599,144	10	5,551,428	9	9.3
1,2,4-trimethylbenzene	581,969	10	5,022,406	8	8.6
m-dichlorobenzene	1,585,358	18	7,488,063	7	4.7
p-dichlorobenzene	1,658,218	16	7,565,648	6	4.6
o-dichlorobenzene	1,442,744	15	6,976,500	7	4.8
1,2,4-trichlorobenzene	2,430,435	18	5,739,457	10	2.4
Hexachloro-1,3-butaiene	914,020	27	4,424,477	8	4.8
Average		21%		26%	8

Table 4-5: Average Extraction Efficiencies For 0.1 L/min and 10 L/min with Relative Standard Deviations and Increase in Compound Extraction
NA – RSDs not available due to non-detects in two of the three samples at 0.1 L/min.
All RSDs Greater than 25% are shaded.

Durability was defined as how well the device maintained its physical structure throughout the study. The 65 μm PDMS HSA-SPME polymer coating was stripped from the nickel alloy wire during sampling at ambient temperatures with flow rates of 1.5 L/min. The 30 μm and 15 μm Carboxen/PDMS HSA-SPME devices were capable of high volume sampling. The outer glass tube provided adequate protection for the device and withstood over 150 connections and disconnections to and from pumps and instrumentation. The electrical wire components were perhaps the most vulnerable portion of the HSA-SPME device, however, it too withstood all the connections and disconnections with Tygon tubing.

5 Discussion and Conclusions

5.1 HSA-SPME Air Sampling Device

This study was intended to evaluate the prototype HSA-SPME Air Sampling Device and its ability to rapidly collect high volume air samples for the detection of trace level VOCs. The HSA-SPME was evaluated in terms of compound extraction efficiency, device desorption efficiency, and total compound uptake per unit time. The unique design of the HSA-SPME device offered a larger polymer surface area and a better contact time with the sample as opposed to traditional SPME fibers. Six flow rates from 0.1 L/min to 10 L/min were evaluated. These flow rates equate to a velocity through the annular space of 28 cm/sec (0.63 mph) to 2807 cm/sec (63 mph), respectively. Two different HSA-SPME polymer types (PDMS and Carboxen/PDMS) were evaluated during this study using a diverse mix of 39 VOC compounds at a concentration of 10 ppb_v.

The PDMS HSA-SPME device was unable to continue through the study because the PDMS polymer was stripped from the nickel alloy wire. This weakness in the adhesion of the polymer coating was most likely due to the winding process of the wire during manufacture. It is possible that this polymer could be used if the polymer was applied to the wire after the wire was wound into a helical shape.

Desorption efficiencies for a 2-second desorption cycle averaged 93% for the Carboxen/PDMS HSA-SPME device. The average desorption efficiency for the PDMS HSA-SPME device was only 54%. Better temperature control and timing during the desorption process would likely improve these efficiencies to near 100%; comparable to

traditional SPME fibers. Near 100% desorption is desirable as it will allow repeated field sampling without carry over from the same device.

The Carboxen/PDMS HSA-SPME device was able to withstand flow rates up to 10 L/min. Yet, the Carboxen/PDMS HSA-SPME device did not perform as theory would suggest. It was anticipated that the higher flow rates would yield a higher extraction efficiency because the boundary layer against the polymer was reduced. However, the higher flow rates (10 L/min) also had less contact time between the air sample and the polymer. This competing factor apparently outweighed the possible increase due to a thinner boundary layer. The extraction efficiency was also well correlated to the boiling point of the compound.

Even though the extraction efficiencies at the higher flow rates were lower, a larger volume of air could be passed across the polymer in the same amount of time. Overall, the higher flow rate was able to extract more mass of material in the same amount of time. Using a constant sampling time of 10 seconds, the highest flow rate of 10 L/min demonstrated an average 8-fold increase in compound uptake over the lowest flow rate of 0.1 L/min.

5.2 Applications

The HSA-SPME device offers a viable substitute for passive SPME fiber sampling. Coated with identical polymer materials, the HSA-SPME device can perform in the same air sampling scenarios where SPME fibers have proven effective. In fact, the HSA-SPME device performance will likely exceed traditional SPME fibers in sensitivity and speed, because of the higher surface area and ability to concentrate large volumes of air

on the polymer. The HSA-SPME Air Sampling Device could prove useful in monitoring for trace level CWAs, explosives, and toxic industrial compounds, as well as perform more rapid crime scene investigations.

5.3 Study Limitations

The HSA-SPME devices were prototypes and the number of devices available were limited. The number of samples and desorptions accomplished throughout this study may have degraded the HSA-SPME devices' performance. Additional HSA-SPME devices would have allowed a maximum on the number of samples and desorptions per device to ensure results were not hindered by degradation.

All sampling was performed at room temperature. All attempts were made to control the environmental conditions; however, due to Heating, Ventilation, Air Conditioning system malfunctions, the room temperature where the samples were collected, varied by as much as 11^{o}C/day. The room environment for the Entech Agilent system was more consistent near 24^{o}C.

5.4 Future Work

The HSA-SPME device has proven successful at rapid, high volume air sampling for trace level VOCs; however, the device is still a prototype with potential for improvement and areas for study. The following list contains several areas of potential research for the HSA-SPME device.

1. HSA-SPME Device Design: Different structural designs to the HSA-SPME device could improve the extraction efficiency at the higher linear velocities. Additional bends, curves or baffles in the annular space of the design may increase the turbulent flow and subsequently improve extraction efficiency. The straight glass tube may not be taking full advantage of flow direction changes that could improve compound uptake.

2. Improve Desorption Process: The 24V manual circuit switch used for desorbing compounds from the HSA-SPME device was a limitation to this study. The goal was rapid, resistive heating to quickly desorb the compounds. However, the process was not well controlled; possibly either leaving compounds absorbed to the polymer or damaging the polymer from extensive heat. A means to automatically control desorption, based on temperature limits, would improve the desorption consistency and likely prolong the usefulness of the HSA-SPME device.

3. Variability Between HSA-SPME Devices: Testing the repeatability between HSA-SPME devices with the same characteristics would be beneficial. The HSA-SPME device is based on SPME fibers and should perform as consistently as SPME fibers with all variables, such as concentration, sampling time, flow rates, etc, held constant.

4. Determine Airborne Concentrations: Given that the HSA-SPME devices perform in a repeatable manner, it may be possible to quantify concentrations of airborne chemicals.

5. Test Compound Adsorption Stability: Field sampling requires a sampling technique that is capable of maintaining sample integrity (no loss of sample, no additional contamination). SPME fibers have been shown to maintain good sample integrity up to 3 days (Pawliszyn 1997), and with a good field design, the HSA-SPME device should be able to do the same. This would also allow for an array of HSA-SPME devices to be used at once. Samples could be stored for later confirmation.

Appendix A

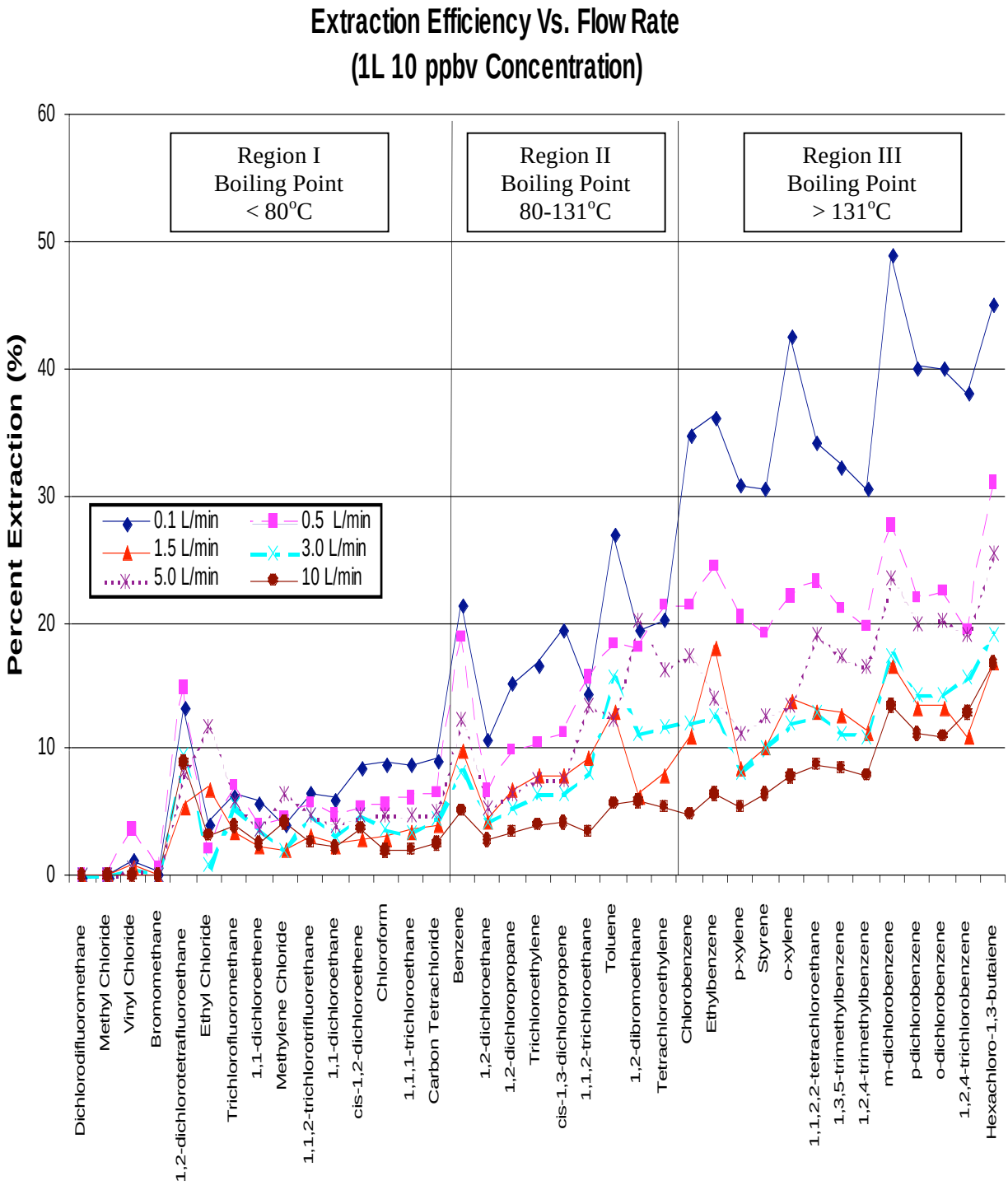


Figure A-1: Extraction Efficiency For VOCs at Flow Rates of 0.1, 0.5, 1.5, 3, 5, and 10 L/min

Appendix B

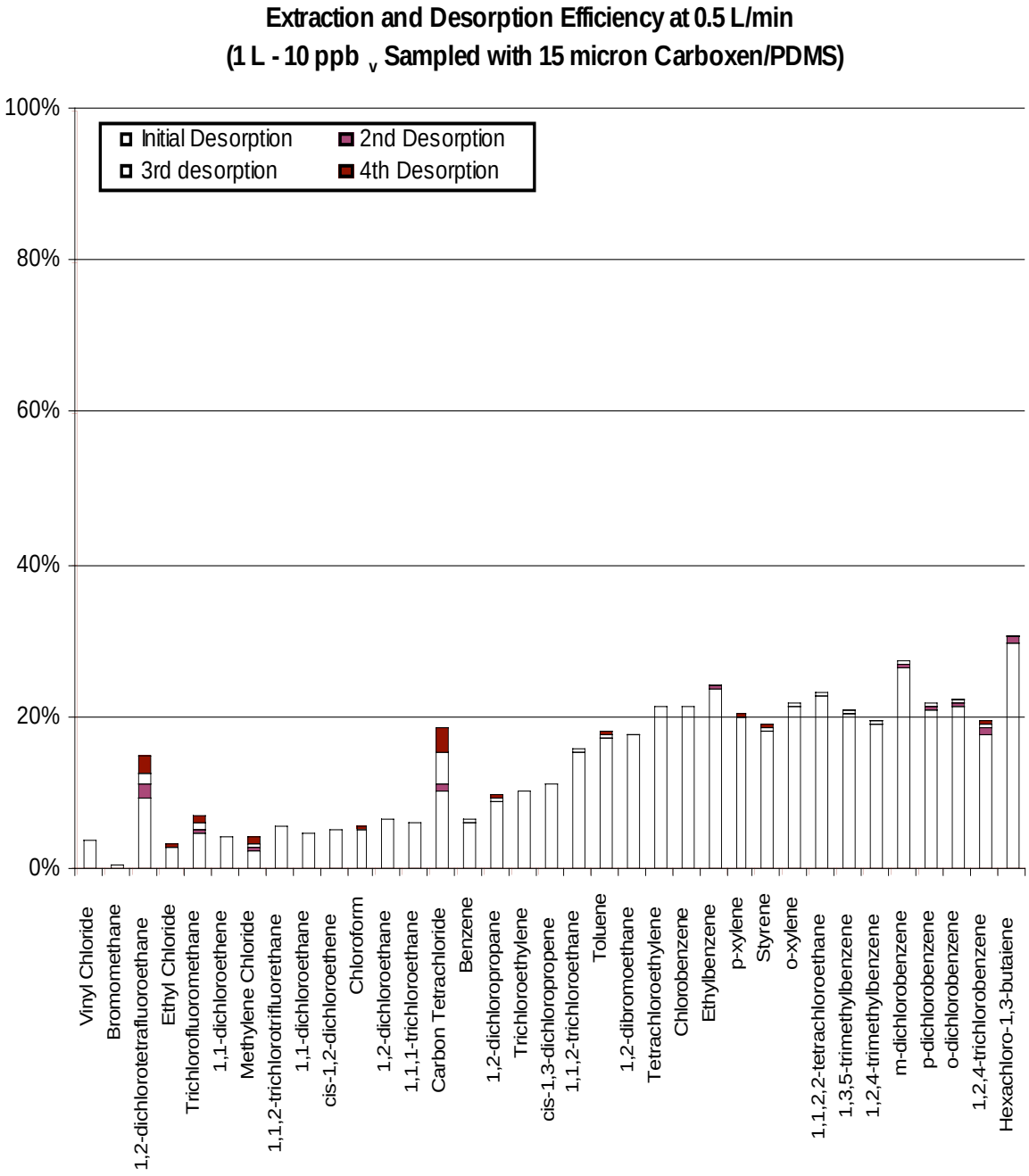


Figure B-1: Extraction Efficiencies For VOCs at a Flow Rate of 0.5 L/min

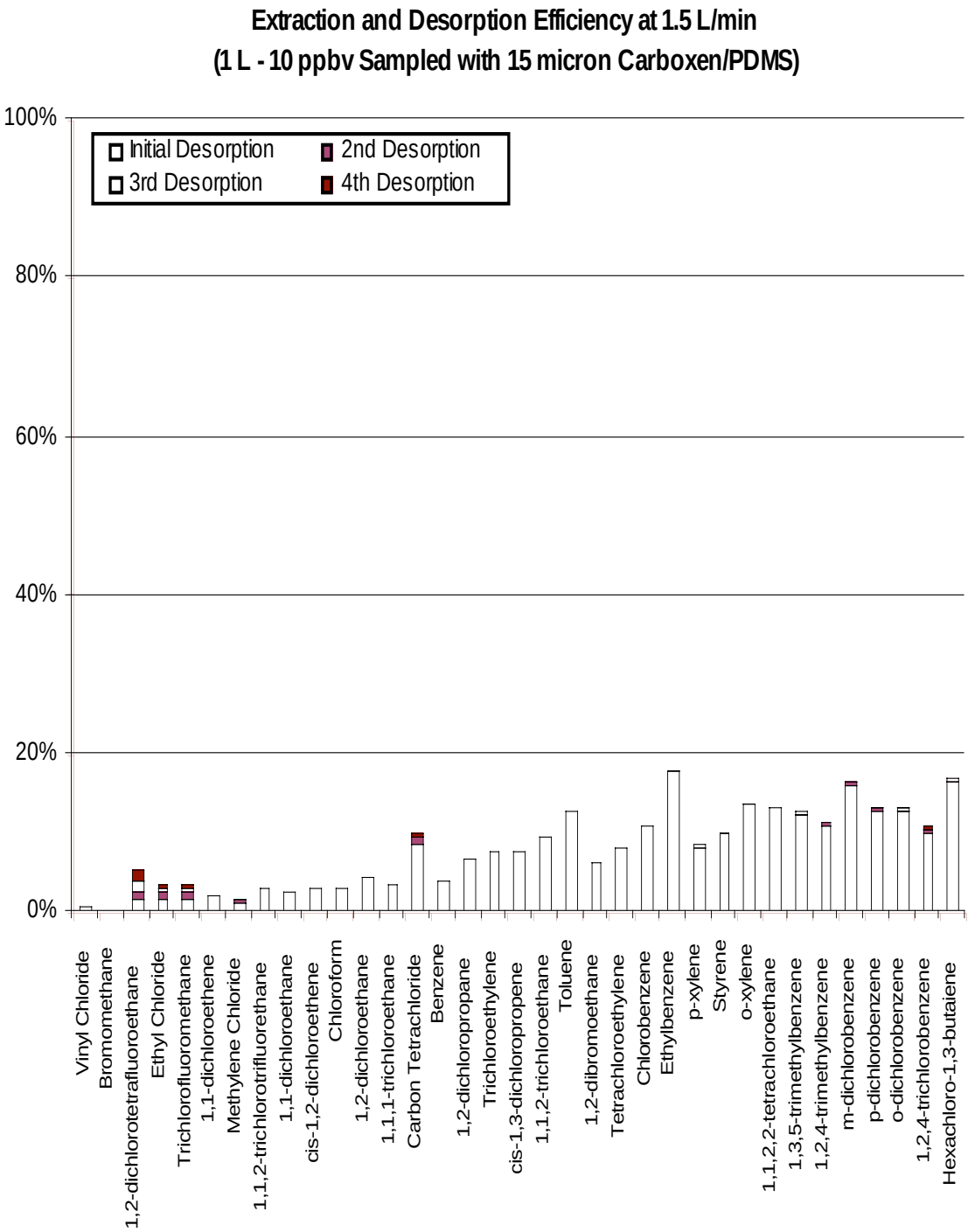


Figure B-2: Extraction Efficiencies For VOCs at a Flow Rate of 1.5 L/min

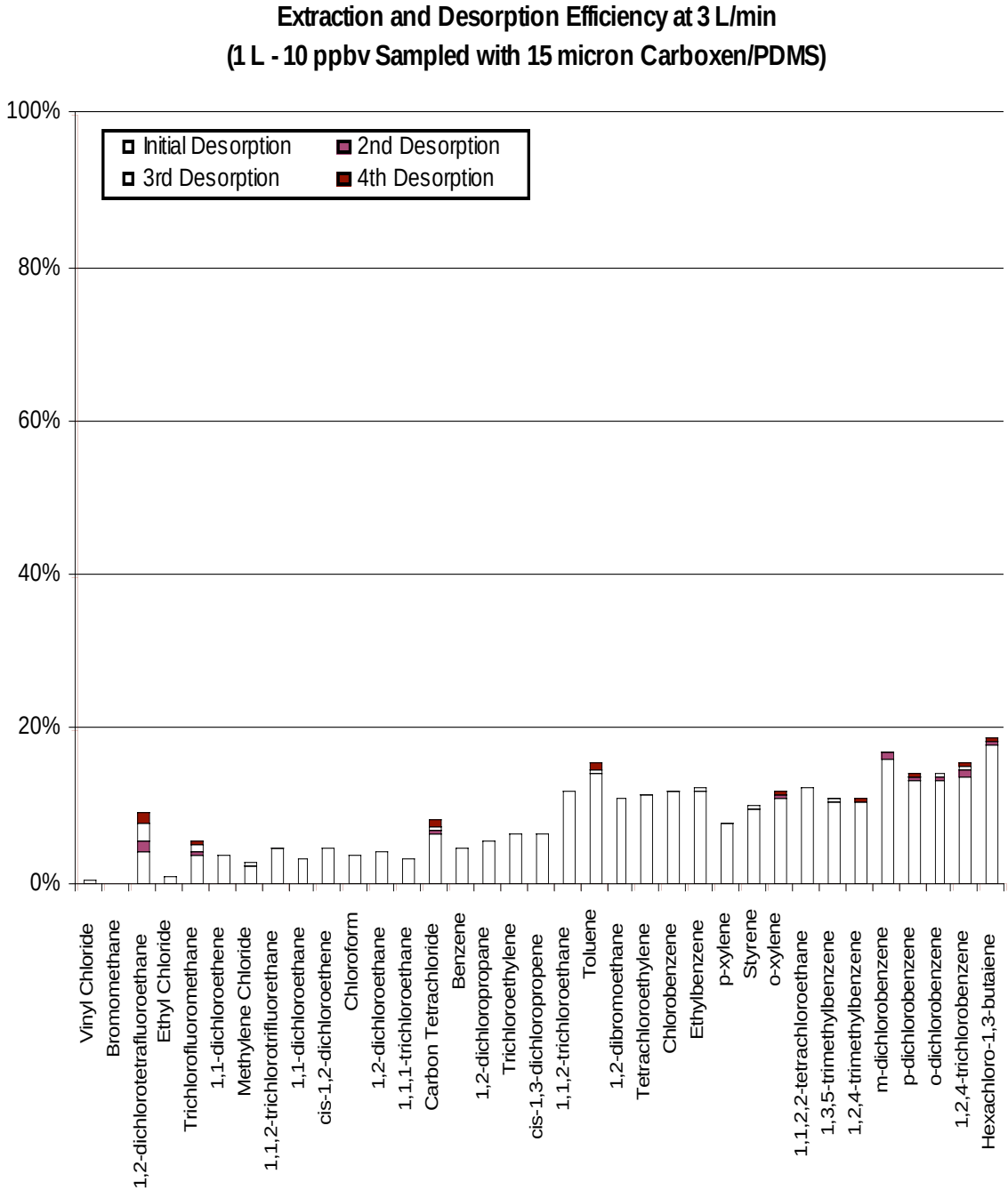


Figure B-3: Extraction Efficiencies For VOCs at a Flow Rate of 3 L/min

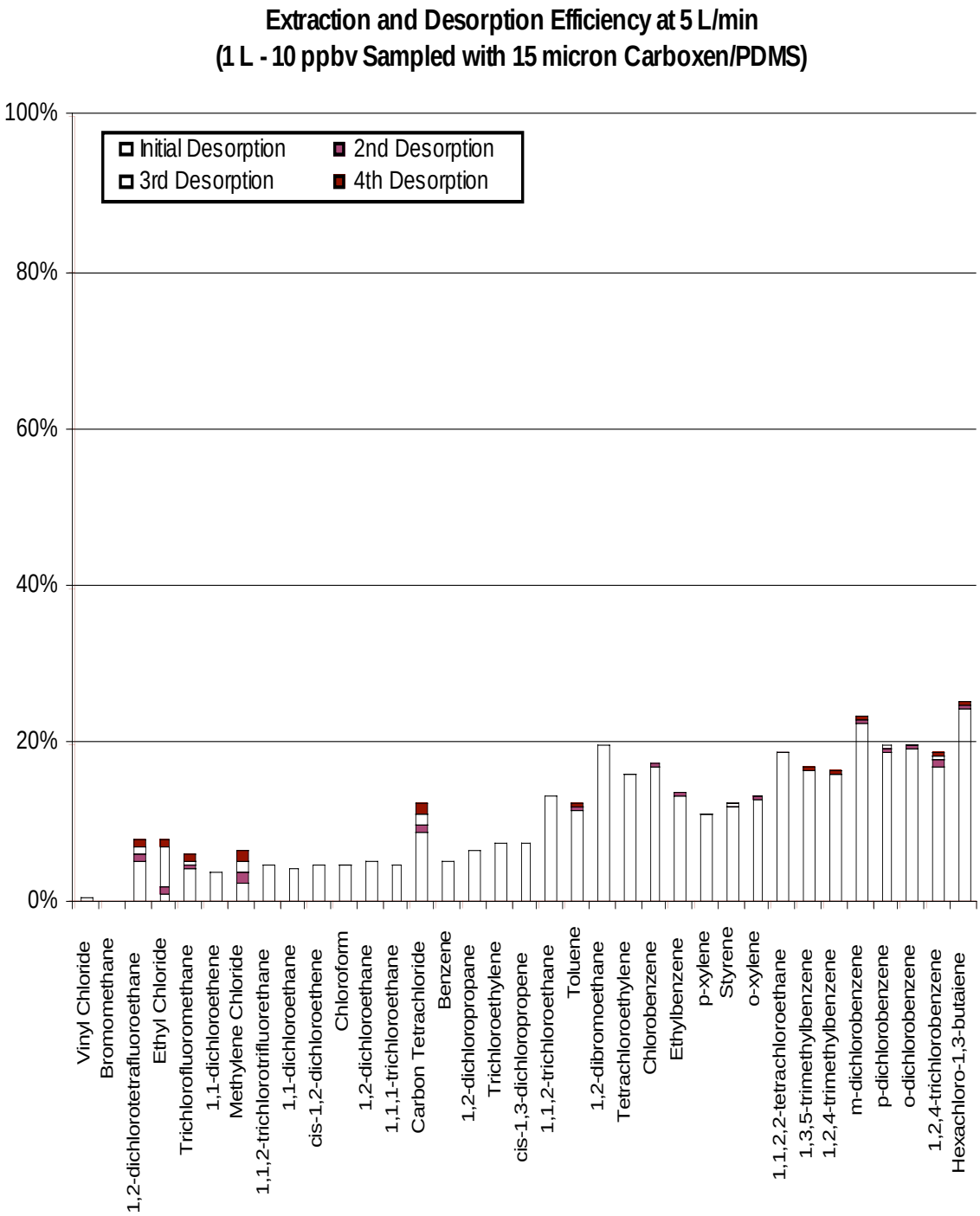


Figure B-4: Extraction Efficiencies For VOCs at a Flow Rate of 5 L/min

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Curriculum Vitae
Shannon Scott McDonald, Major, USAF, BSC

Major Shannon "Scott" McDonald was born in Blackwell, Oklahoma on March 23, 1973. A son of a successful military mother, Jolene McDonald, Major McDonald joined the US Air Force on 18 Jun 1991, as he accepted his appointment to the United States Air Force Academy. Graduating with a Bachelor of Science Degree in Environmental Engineering in 1995, Major McDonald started his first tour of duty as a Bioenvironmental Engineer at Keesler AFB, Biloxi, MS., as the Officer-in-Charge of Environmental Compliance. Following his three years at Keesler AFB, Major McDonald traveled to Patrick AFB and Cape Canaveral Air Station, FL., and assumed responsibility for the Wing's Occupational Health Program and oversaw the successful launch of Titan, Delta, and Atlas rockets. In 2001, Major McDonald transferred to Buckley AFB in Denver, CO., to establish a new Bioenvironmental Engineering Flight at the Air Force's newest Wing. During his tour of Buckley AFB, Major McDonald took command of his first Aerospace Medicine squadron. In 2004, Major McDonald was accepted into the Master of Science in Public Health program at the Uniformed Services University of the Health Sciences, National Naval Medical Center, Bethesda, MD. Upon completion of his MSPH degree, Major McDonald will be traveling to Brooks City-Base in San Antonio, TX., and assume the role of Industrial Hygiene consultant for the Air Force.

Major McDonald married Jennifer L. Crabtree in 1996, and has three children, Samantha, Alex, and Jessica.